APPLICATIONS OF GROUP THEORY
IN
SOLID STATE PHYSICS

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CONTENTS

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ABSTRACT

Recent progress in the theory of generalized 6j symbols and 3jm factors has led to a building up method of calculation which uses only character theory results. This thesis both extends the method and uses 3jm factors in several solid state applications.

We compute tables of transformation coefficients between the standard angular momentum basis and various point group bases. These coefficients are used to show that some of the phase freedoms in the 3jm factors affect the orientation of the point group axes. Tables of 6j symbols for SU_6 and SU_3 and 3jm factors for $SU_6 \supset SU_2 \times SU_3$, $SU_3 \supset U_1 \times SU_2$ and $SU_3 \supset SO_3$ have also been computed for use in multiquark hadron calculations and in strong crystal field calculations.

The example of Re^{3+} ions in tetragonal (C_{4v}) CaF_2 sites is used to illustrate the advantages of point group 3jms. The use of a point group basis results in more natural parameters, and basis states which are not greatly mixed by the Hamiltonian. For some ions the data are sparse or contradictory but for others the crystal field parameters follow a smooth trend. The superposition model is used to calculate co-ordination angles for these ions and the results are consistent with endor experiments. Intensity calculations for Er^{3+} are in reasonable agreement with experiment.

Pair interactions are studied in point group bases. A general prescription is given for constructing pair states from single-ion states and general results are derived for pairs of identical Kramers ions.

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CHAPTER 1

INTRODUCTION

Group theory has played an important role in the application of quantum mechanics to physical systems. The work of Racah (1941 - 1949) and Wigner (1940, 1959) provided powerful mathematical tools, without which many subsequent calculations would have been impossible. Group representations provide us with convenient labels for the states and operators. The familiar quantum numbers J and M refer to the irreducible representations (irreps) of SO_3 (or R_3) and SO_2 and these groups provide a suitable basis for calculations involving free atoms.

When an atom is in an anisotropic situation, in a crystal or a molecule, it is more natural to use a chain of groups which reflect the exact and approximate symmetries of the site. Recent advances in the techniques for calculating 6j symbols and 3jm factors of arbitrary groups using the building up method (Butler and Wybourne 1976a) have led to the computerized generation of tables for all point groups (Butler 1981). A crystal field or molecular Hamiltonian is more diagonal in the appropriate point group basis than in the JM basis. The basis states are therefore more physical because they are approximate eigenstates of the Hamiltonian.

Quantum mechanical calculations of energy levels and transition probabilities involve the computation of matrix

elements of tensor operators. The Wigner-Eckart theorem is the group theoretic tool which factorizes matrix elements into a part which depends on the transformation properties of the operator and states and a part which does not (the reduced matrix element). The Wigner-Eckart theorem may be applied to any group and if we know the appropriate j and jm symbols we may calculate matrix elements in the basis of our choice.

Energy levels of Re^{3+} ions in tetragonal (C_{4v}) sites in CaF_2 are computed in chapter 5. Calculations for all Re^{3+} ions (except Gd^{3+}) are performed and compared with experimental results. The superposition model (Newman 1971) is used to analyse the crystal field parameters and estimates of the local distortions of the sites are made. For some ions the parameters are inconsistent with the superposition model. In most of these cases the data from various sources are inconsistent and it is suggested that some data has been misinterpreted.

Intensity calculations are considered in chapter 6. Newman and Balasubramanian's (1975) discussion of the generality of the low temperature intensity parameters is clarified by the use of point group methods. Calculations are performed for Er^{3+} in CaF_2 and these are found to be in reasonable agreement with experiment.

Pair interactions are discussed in chapter 7. The construction of pair states from single ion states is shown to be quite straightforward and several general results are derived for pairs of identical ions.

In addition to these applications some work of a more mathematical nature is presented. The orientation phase problem discussed in chapter 3 (and appendix 1), is important in understanding the phase choices which are made when calculating 3jm factors by the building up method. This work is also useful for applications because one sometimes needs to know the orientation of the symmetry axes and mirror planes of a group scheme or the transformation properties of various orientations of the Zeeman operator (chapter 5) or electric dipole operator (chapter 6).

The building up method of calculating 3jms and 6js is quite general and may be used not only for all point groups but also for continuous groups. Tables of 3jms and 6js for SU_6 and SU_3 were computed in a joint effort involving four other members of this department (appendix 2). Orientation-type phase choices occur for each of the 3jm factor tables. These tables have many applications. The $SU_6 \supset SU_2 \times SU_3$ 3jm factors have been used for multi-quark hadron calculations (Bickerstaff and Wybourne 1980, 1981, Black and Wybourne 1981) and the $SU_3 \supset SO_3$ 3jms have been used by Butts (1981) for crystal field calculations in the strong field parentage scheme. The computer programs I wrote to calculate matrix elements using the Wigner-Eckart theorem are also quite general: some of the multiquark hadron dissociation calculations of Black and Wybourne (1981) were performed by these programs.

CHAPTER 2

GROUP THEORY BACKGROUND

The use of 3jm and 6j symbols in the calculation of matrix elements of tensor operators dates back to the work of Wigner (1940, 1959) and calculations using the Wigner-Eckart theorem in the JM basis of SO_3 (Rotenberg et al. 1959) are now common. Groups other than $SO_3(J)$ and $SO_2(M)$ are also useful. Racah (1949) used larger groups to classify and construct the electronic states of rare earth ions and Tanabe et al. (1954-1956) applied his methods to transition metal ions in crystals.

Though the symmetric 3jm and 6j symbols may be defined for any group (Derome and sharp 1965, Butler 1975) many authors still calculate coupling and recoupling coefficients. For example, Kustov (1977) for SU_3, So and Strottman (1979) for SU_6. 3jm and 6j symbols, being more symmetric, are easier to calculate and more compact to tabulate. Butler and Wybourne (1976a) have introduced a method of calculation which requires only a knowledge of character theory, chiefly product and branching rules. These methods have been used to construct tables for all point groups (Butler 1981) and have also been applied to the exceptional Lie groups (Butler, Haase and Wybourne 1978, 1979), where the large dimensionality of the irreps rules out methods which require construction of the irrep matrices.

This chapter contains a summary of the more important definitions we shall need. The reader is referred to Butler

(1981) for further details. Many of the results quoted in this chapter are generalizations of equations appearing in Judd (1963) and Wybourne (1965).

(2.1) j and jm symbols

We use Dirac's notation to label a basis ket $|x\lambda i\rangle$. λ is an irrep of the group, G, i distinguishes its partners and the additional label x distinguishes states with the same transformation properties. In our applications the irrep labels of subgroups of G will replace the single label i. Such a subgroup scheme must extend to a group in which all irreps are one-dimensional (e.g. a cyclic group) to distinguish the partners of λ. The JM basis of SO_3 fulfills this criterion.

The jm and j symbols are related to coupling and recoupling coefficients. We use the definitions of Butler (1981), which are sufficient for all the groups we shall need to consider but require extension for groups which are not simple-phase (see Butler 1975).

jm Symbols

The 3jm symbol is defined by

$$\begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \ell_1 & \ell_2 & \ell_3 \end{pmatrix}^{r} = \sum_{\ell} \langle 0 | \lambda_3^* \ell_3^*, \lambda_3 \ell_3 \rangle \langle r \lambda_3^* \ell_3^* | \lambda_1 \ell_1, \lambda_2 \ell_2 \rangle H(\lambda_1 \lambda_2 \lambda_3^*) \tag{2.1.1}$$

where r is a product multiplicity index which is necessary if $\lambda_1 \times \lambda_2$ contains λ_3^* more than once. The factor $H(\lambda_1 \lambda_2 \lambda_3^*)$

may be chosen unity but for historical reasons a phase

$$H(H_1J_2J_3) = (-)^{J_1-J_2+J_3} \tag{2.1.2}$$

is conventional when the group is SO_3. A 2jm symbol is defined by

$$\begin{pmatrix} \lambda_1 & \lambda_2 \\ \ell_1 & \ell_2 \end{pmatrix} = |\lambda_1|^{\frac{1}{2}} <0|\lambda_1\ell_1, \lambda_2\ell_2> \tag{2.1.3}$$

The 2jm may be chosen diagonal and real (Butler 1975) and so we may represent it by

$$\begin{pmatrix} \lambda \\ \ell \end{pmatrix} = \begin{pmatrix} \lambda\lambda^* \\ \ell\ell^* \end{pmatrix} = \begin{pmatrix} \lambda\lambda^*0 \\ \ell\ell^*0 \end{pmatrix} |\lambda|^{\frac{1}{2}} = \pm 1 \tag{2.1.4}$$

We may then rewrite 2.1.1 as

$$\begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ \ell_1 & \ell_2 & \ell \end{pmatrix} r = |\lambda|^{-\frac{1}{2}} \begin{pmatrix} \lambda^* \\ \ell^* \end{pmatrix} <r\lambda^*\ell^*|\lambda_1\ell_1, \lambda_2\ell_2> H(\lambda_1\lambda_2\lambda^*) \tag{2.1.5}$$

For a group chain the symbols may be factorized:

$$\begin{pmatrix} \lambda \\ a \\ \mu \\ i \end{pmatrix} G \\ H = \begin{pmatrix} \lambda \\ a \\ \mu \end{pmatrix} G \\ H \begin{pmatrix} \mu \\ i \end{pmatrix} H \tag{2.1.6}$$

$$\begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ a_1 & a_2 & a_3 \\ \mu_1 & \mu_2 & \mu_3 \\ i_1 & i_2 & i_3 \end{pmatrix} rG \\ H = \sum_s \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ a_1 & a_2 & a_3 \\ \mu_1 & \mu_2 & \mu_3 \end{pmatrix} rG \\ sH \begin{pmatrix} \mu_1 & \mu_2 & \mu_3 \\ i_1 & i_2 & i_3 \end{pmatrix} sH \tag{2.1.7}$$

where the a labels are branching multiplicity labels for $G \supset H$.

j symbols

The nj symbols are independent of basis. The 2j, $\{\lambda\lambda^*\}$ or $\{\lambda\}$, gives the permutation properties of the 2jm and the 3j $\{\lambda_1\lambda_2\lambda r\}$ gives the column interchange symmetry of the 3jm (Butler and Wybourne 1976a). Both the 2j and 3j symbols are chosen real. The 6j symbols are defined by:

$$\begin{Bmatrix}\lambda_1 & \lambda_{23} & \lambda^* \\ \lambda_3 & \lambda_{12} & \lambda_2\end{Bmatrix}_{r_{12}r_{23}rs} = |\lambda_{12}|^{-\frac{1}{2}}|\lambda_{23}|^{-\frac{1}{2}}\{\lambda_2\}\{\lambda_{12}\lambda_3\lambda^* r\}\{\lambda_1\lambda_2\lambda_{12}r_{12}\}$$

$$\times \langle(\lambda_1\lambda_2)r_{12}\lambda_{12}\lambda_3 r\lambda|\lambda_1(\lambda_2\lambda_3)r_{23}\lambda_{23},s\lambda\rangle \qquad (2.1.8)$$

and the 9j by:

$$\begin{Bmatrix}\lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3\end{Bmatrix}\begin{matrix}r_1 \\ r_2 \\ r_3\end{matrix} = |\lambda_3|^{-\frac{1}{2}}|\mu_3|^{-\frac{1}{2}}|\nu_1|^{-\frac{1}{2}}|\nu_2|^{-\frac{1}{2}}$$

$$\begin{matrix}s_1 & s_2 & s_3\end{matrix}$$

$$\times \langle(\lambda_1\lambda_2)r_1\lambda_3^*(\mu_1\mu_2)r_2\mu_3^*,s_3\nu_3|(\lambda_1\mu_1)s_1\nu_1^*(\lambda_2\mu_2)s_2\nu_2^*,r_3\nu_3\rangle \qquad (2.1.9)$$

Properties of j and jm Symbols

Because they are related to the elements of unitary matrices the j and jm symbols obey 'orthonormality' conditions. They also have symmetries under column interchange and complex conjugation (Butler and Wybourne 1976a, Butler 1981). These properties are generalizations of the familiar 3j and 6j symbols

for $SO_3 \supset SO_2$ tabulated in Rotenberg et al (1959). Additional relationships are useful for calculating the symbols (See Section 3.1 and Appendices 1 and 2).

The j symbols and jm factors are nonzero only if certain 'triad' conditions are satisfied. $(\lambda_1\lambda_2\lambda_3 r)$ 'is a triad' if $\lambda_1 \times \lambda_2$ contains λ_3^*. The multiplicity label r is necessary if $\lambda_1 \times \lambda_2$ contains λ_3^* more than once. It is obvious from their definitions that the rows of a 3jm factor and the rows and columns of a 9j form triads. For the 6j symbol the triads are

(2.1.10)

In our calculations of 3jm factors and 6j symbols the concept of power is used. We choose a faithful irrep and call it the "primitive" irrep, ϵ. For SO_3, SO_2 and the point groups the primitive is always chosen to be $\frac{1}{2}$. For SU_3 and SU_6 the primitive is 1. The power of an irrep λ is the smallest p for which the product $(\epsilon + \epsilon^*)^p \supset \lambda$. The power of the identity irrep, which we always denote as 0, is zero. The building up method of calculation which was developed by Butler and Wybourne (1976a) proceeds by calculating 6j symbols for group and subgroup and then 3jm factors for the branching. Phase choices must be made during the calculation and a special class of these will be discussed in chapter 4.

(2.2) Transformation coefficients

Transformation coefficients have been used to calculate 3jms (or coupling coefficients) (e.g. Golding 1971, Kibler and Chatterjee 1978). We work the other way round and calculate transformation coefficients from 3jm symbols. The equation

$$\langle \lambda i | \lambda \ell \rangle' = \sum_{i_1 i_2 \ell_1 \ell_2} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ i_1 & i_2 & i \end{pmatrix}^{*r} \langle \lambda_1 i_1 | \lambda_1 \ell_1 \rangle'^{*} \langle \lambda_2 i_2 | \lambda_2 \ell_2 \rangle'^{*} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ \ell_1 & \ell_2 & \ell \end{pmatrix}^{'r} |\lambda| \qquad (2.2.1)$$

may be used recursively, choosing λ_1 to be the primitive irrep so that only primitive 3jm symbols are needed. The transformation between the partners of the primitive irrep involves a choice, which corresponds to the relative orientation of the axes (see chapter 4 and appendix 1).

(2.3) The Wigner-Eckart Theorem

The Wigner-Eckart theorem is the connection which allows us to use group theory to make quantitative calculations. The theorem factorizes the matrix elements of an irreducible tensor operator T^{λ}_{ℓ} which has well defined transformation properties under the particular group-subgroup scheme.

$$\langle x_1 \lambda_1 \ell_1 | T^{\lambda}_{\ell} | x_2 \lambda_2 \ell_2 \rangle = \sum_r \begin{pmatrix} \lambda_1 \\ \ell_1 \end{pmatrix} \begin{pmatrix} \lambda_1^* & \lambda & \lambda_2 \\ \ell_1^* & \ell & \ell_2 \end{pmatrix}^r \langle x_1 \lambda_1 \| T^{\lambda} \| x_2 \lambda_2 \rangle_r \qquad (2.3.1)$$

The last term on the right is known as the 'reduced matrix element' and its value is dependant on information other than transformation properties, which have been 'factored out' by the jm symbols.

Eqn. 2.3.1 may be factorized to give

$$\langle x_1\lambda_1 a_1\sigma_1 \| T^{\lambda a\sigma} \| x_2\lambda_2 a_2\sigma_2\rangle^{H}_{s}$$

$$= \sum_r \begin{pmatrix} \lambda_1 \\ a_1 \\ \sigma_1 \end{pmatrix} G \begin{pmatrix} \lambda_1^* & \lambda & \lambda_2 \\ a_1^* & a & a_2 \\ \sigma_1^* & \sigma & \sigma_2 \end{pmatrix} rG \langle x_1\lambda_1 \| T^{\lambda} \| x_2\lambda_2\rangle^{G}_{r} \qquad (2.3.2)$$

Coupled Tensors

Many quantum-mechanical interactions are described in terms of coupled products of tensors. If both tensors act on the same space we have a generalization of eqn. 3.39 of Judd (1963)

$$\langle x_1\lambda_1 \| \{P^{K_1}Q^{K_2}\}^{rK} \| x_2\lambda_2\rangle_s$$

$$= \sum_{x_3\lambda_3 s_1 s_2} H(K_1K_2K)\,|K|^{\frac{1}{2}}\{\lambda_1\}\{\lambda_1^* K_1\lambda_3 s_1\}$$

$$\{\lambda_3^* K_2\lambda_2 s_2\}\begin{Bmatrix} K_2 & K & K_1 \\ \lambda_1 & \lambda_3 & \lambda_2 \end{Bmatrix}_{s_2 s s_1 r} \langle x_1\lambda_1 \| P^{K_1} \| x_3\lambda_3\rangle_{s_1} \langle x_3\lambda_3 \| Q^{K_2} \| x_2\lambda_2\rangle_{s_2} \qquad (2.3.3)$$

If the tensors act on two (or more) different spaces (e.g. spin and orbital spaces) eqn. 2.3.1 may be used independently on each tensor

$$\langle \lambda_1 \ell_1 \mu_1 i_1 | T^{\lambda}_{\ell} R^{\mu}_{i} | \lambda_2 \ell_2 \mu_2 i_2 \rangle$$

$$= \sum_{rs} \langle \lambda_1 \| T^{\lambda} \| \lambda_2 \rangle_r \begin{pmatrix} \lambda_1 \\ \ell_1 \end{pmatrix} \begin{pmatrix} \lambda_1^* & \lambda & \lambda_2 \\ \ell_1^* & \ell & \ell_2 \end{pmatrix}^r$$

$$\langle \mu_1 \| R^{\mu} \| \mu_2 \rangle_s \begin{pmatrix} \mu_1 \\ i_1 \end{pmatrix} \begin{pmatrix} \mu_1^* & \mu & \mu_2 \\ i_1^* & i & i_2 \end{pmatrix}^s \qquad (2.3.4)$$

Our two spaces may be restricted to one space (e.g. total angular momentum). We represent this in terms of groups by

$$G^S \times G^L \supset G^J$$

The appropriate form of the Wigner-Eckart theorem is then

$$\langle (\lambda_1\lambda_2) r_1 \lambda \| \{P^{\kappa_1} Q^{\kappa_2}\}^{t\kappa} \| (\mu_1\mu_2) r_2 \mu \rangle_s = \sum_{s_1 s_2} H(\lambda_1\lambda_2\lambda) H(\kappa_1\kappa_2\kappa) H(\mu_1\mu_2\mu)$$

$$|\lambda|^{\frac{1}{2}} |\mu|^{\frac{1}{2}} |\kappa|^{\frac{1}{2}} \begin{Bmatrix} \lambda_1 & \lambda_2 & \lambda^* \\ \kappa_1^* & \kappa_2^* & \kappa \\ \mu_1^* & \mu_2^* & \mu \\ s_1 & s_2 & s \end{Bmatrix}^{r_1}_{t}_{r_2} \langle \lambda_1 \| P^{\kappa_1} \| \mu_1 \rangle_{s_1} \langle \lambda_2 \| Q^{\kappa_2} \| \mu_2 \rangle_{s_2} \qquad (2.3.5)$$

If one of κ_1, κ_2 or κ is the identity the 9j may be reduced to a 6j by

$$\begin{Bmatrix} \lambda_1 & \lambda_2 & \mu \\ \lambda_3 & \lambda_4 & \mu^* \\ \nu & \nu^* & 0 \\ r_3 & r_4 & 0 \end{Bmatrix}^{r_1}_{r_2}_{0} |\mu|^{-\frac{1}{2}} |\nu|^{-\frac{1}{2}} \{\lambda_2\}\{\nu\}\{\lambda_2\lambda_4\nu^* r_4\}\{\lambda_3\lambda_4\mu^* r_2\}$$

$$\times \begin{Bmatrix} \lambda_1 & \lambda_3 & \nu \\ \lambda_4 & \lambda_2^* & \mu \end{Bmatrix}_{r_1 r_2 r_4 r_3} \qquad (2.3.6)$$

and equations 3.37 and 3.38 of Judd (1963) can be derived if the appropriate reduced matrix element for the unit operator is substituted. (Note that it is not necessarily unity).

The only other type of branching we might want to consider is of the form

$$G \supset H \times L \qquad (2.3.7)$$

which is easily treated by considering the direct product group H x L to be a single subgroup of G.

CHAPTER 3

GROUP THEORETIC CALCULATIONS

The tables in Butler (1981) were generated by computer and many of the calculations described in this thesis were performed by extensions of his programs. A preliminary version of these routines was described in Reid (1979) but since then many modifications and extensions have been made. A discussion of the details of the computational routines will not be given because they are not machine-independent (since they are written in Burrough's Extended Algol) and are in a state of continuous development. Instead I shall give a brief description of the methods used, which will serve as background to later chapters.

(3.1) 6j symbols and 3jm factors

Butler's program constructs and calculates 6j symbols and 3jm factors using exact arithmetic routines, the results appearing as complex surds. The avoidance of floating-point numbers makes the program more useful for investigation of the properties of the coefficients, makes checking of results easier and aids hand calculations. For the calculation of 3jms and 6js for the continuous groups SU_3 and SU_6 (Appendix 2), modifications were made to the procedures described by Butler and Wybourne (1976a) and used to construct the tables of Butler (1981). These modifications are described in detail by Bickerstaff and Wybourne (1981) and Bickerstaff (1980). The major change is the use of

different forms of the Biedenharn-Elliott sum rule for 6js (Butler and Wybourne 1976a eqn 20) and the Wigner formula for 3jms (Butler and Wybourne 1976a eqn 40) so as to be able to calculate all coefficients up to a particular power without requiring any of higher power. These modifications to the program were made by R W Haase. For computation of 3jm factors with product-group subgroups, such as $SU_6 \supset SU_2 \times SU_3$ and $SU_3 \supset U_1 \times SU_2$ (appendix 2), I modified the program so that the two subgroup 6j tables could be used, rather than construct a new table. For product groups a 6j symbol may be factorized

$$\left\{\begin{matrix}\lambda_1\times\mu_2 & \lambda_2\times\mu_2 & \lambda_3\times\mu_3\\ \lambda_4\times\mu_4 & \lambda_5\times\mu_5 & \lambda_6\times\mu_6\end{matrix}\right\}^{G\times H}_{r_1s_1\ r_2s_2\ r_3s_3\ r_4s_4}$$

$$= \left\{\begin{matrix}\lambda_1 & \lambda_2 & \lambda_3\\ \lambda_4 & \lambda_5 & \lambda_6\end{matrix}\right\}^{G}_{r_1r_2r_3r_4} \left\{\begin{matrix}\mu_1 & \mu_2 & \mu_3\\ \mu_4 & \mu_5 & \mu_6\end{matrix}\right\}^{H}_{s_1s_2s_3s_4} \qquad (3.1.1)$$

but note that the 6js of the product group contain more freedom than the product of 6js so a set of arbitrarily chosen 6js for GxH is not necessarily factorizable. For example $U_n = U_1 \times SU_n$ but an arbitrary choice of U_n symbols will not factorize (e.g. So and Strottman's 1979 U_6 tables).

A similar result applies to 3jm factors. 3jm factors for $G \supset K$ have more freedom than those for $G \supset H \supset K$ (i.e. a product of $G \supset H$ and $H \supset K$ factors). Butler and Reid (1979) showed that the usual choice of phase for $SO_3 \supset SO_2$ does not allow the insertion of D_∞ in the chain and showed how to change the choices to make this possible.

There are two very good reasons for using factorization as much as possible. Firstly the tables are smaller and secondly multiplicity is often resolved by the irrep labels of the extra groups, thus simplifying the calculations. If possible the intermediate groups should be chosen to have some physical significance. In chapter 5 we use the octahedral group as an intermediate group since the tetragonal CaF_2 sites considered there are basically cubic, with an interstitial reducing the symmetry to C_{4v}. For some C_{4v} sites $D_{\infty h}$ would be a better intermediate group (see, for example, Grenet et al 1980).

(3.2) Transformation Coefficients

I used equation (2.2.1) and the relationship between odd and even parity coefficients (appendix 4) to calculate transformations between point group bases of O_3 (= SO_3 x C_i) and the JM basis and between bases of point-groups. Some of these tables appear in Butler (1981). The transformation coefficients were essential in elucidating the 'orientation phase' problems discussed in chapter 4 and appendix 1. They are necessary to compare our crystal-field parameters with those of other authors (Chapter 5) and to deduce the transformation properties of various polarizations of the electric and magnetic dipole operators in intensity calculations (chapter 6). They have also proved useful in other applications: Churcher and Stedman (1981a and b) have used them to calculate selection rules for Raman scattering and

Stedman and Minard (1981) have used them in their work on lattice strain.

(3.3) The Wigner-Eckart Theorem

Equations (2.3.2) and (2.3.5) were implemented to allow calculations of matrix elements of tensor operators for any group chain. The program was tested extensively and used to evaluate matrix elements of the colour-spin operator in the scheme

$$[(SU_6 \supset SU_2 \times SU_3) \times (SU_6 \supset SU_2 \times SU_3)] \times (SU_6 \supset SU_2 \times SU_3)$$
$$\supset (SU_2 \times SU_3) \times (SU_2 \times SU_3) \supset SU_2 \times SU_3 \qquad (3.3.1)$$

These matrix elements were used by Black and Wybourne (1981) in their multiquark hadron dissociation calculations. In comparison to this scheme the group chain used in the crystal field calculations of chapter 5:

$$O_3^S \times O_3^L \supset O_3^J \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4 \qquad (3.3.2)$$

is quite straight-forward.

Our calculations of 3jms and 6js for unitary groups (Bickerstaff et al. 1981, appendix 2) is a first step in assembling enough tables to allow us to calculate matrix elements of electronic states without recourse to the tables of Nielson and Koster (1963). Given the 3jm factors my procedures could be used to calculate matrix elements using the f^n parentage groups:

$$SU_{14} \supset SU_2^S \times (SU_7 \supset SO_7 \supset G_2 \times SO_3^L) \qquad (3.3.3)$$

Tabulations of 3jm factors will be much smaller than Nielson and Koster's tables. Calculations in the 'strong field' parentage scheme for d^n states (Kustov 1977, Butts 1981):

$$U_{10} \supset U_4 \times U_6 \supset (SU_2^S \times U_2^e) \times (SU_2^S \times U_3^{t_2}) \supset SU_2^S \times O \qquad (3.3.4)$$

or for mixed configurations will also be possible. Using the Wigner-Eckart theorem directly, rather than building up via cfps (Racah 1949, Judd 1963) clarifies such calculations.

Given transformation properties of the states and operators and reduced matrix elements of the operators it is straight-forward to work down these group chains, using equation (2.3.2) for branchings of the form $G \supset K$ or $G \supset H \times K$ and (2.3.5) for $G \times G \supset G$. The program only stores non-zero matrix elements and only one copy of states indistinguishable by the group labels used so far (e.g. ^2F under $O_3^S \times O_3^L$). The states are expanded, using tabulated branching and product rules, as the calculation progresses (e.g. to $^2F_{\frac{5}{2}}$ and $^2F_{\frac{7}{2}}$). This is convenient for groups with irreps of large dimension because large matrices are not generated unnecessarily. Indeed, the multiquark hadron calculations were terminated at the $SU_2 \times SU_3$ level, where all operators are scalar. For a scalar operator the phases of the 3jm and 2jm symbols in equation (2.3.1) cancel, requiring only a normalization to convert reduced matrix elements into matrix elements. Physical states are required to be colour singlets, i.e.

transform as $O(SU_3^{colour})$ so any other states were discarded, further reducing the amount of calculation. The same principle was used for the construction of intermediate coupling wave functions used in the $Re^{3+}:CaF_2$ calculations (chapter 5). Since the spin-orbit and coulomb operators are scalar under SO_3^J the calculation is stopped at that level.

CHAPTER 4

ORIENTATION PHASES

The building up method of calculating 6j symbols and 3jm factors uses only character theory results, chiefly product and branching rules. Other methods proceed from explicit definitions of the symmetry axes or the generators of the group so it is not surprising that some of the free phases used in our calculations of 3jm factors correspond to different orientations of point group axes.

We shall use appendix 1 (Reid and Butler 1980) as a starting point. There we have demonstrated the existence of orientation phases and shown how to use transformations from point groups to the JM basis to determine the orientation of the point group axes. This is of some importance for our discussion of crystal field calculations (chapter 5) and intensity calculations (chapter 6). This chapter clarifies some of the ideas expressed in appendix 1 and extends them to rotation-reflection groups and to the unitary group branchings discussed in appendix 2.

(4.1) Orientation phase choices

Many phase and multiplicity choices must be made in the calculation of 6j symbols and 3jm factors. The feature which distinguishes orientation phase choices from other 3jm choices is that transformations between two sets of

3jm factors with different orientation choices require primitive transformation factors which are not unity. In appendix 1 we showed that this restriction is equivalent to a rotation. However, there is a distinction between the 'continuous' orientation choices (e.g. $D_3 \supset C_3$) and the 'double root' choices (e.g. $T \supset D_2$). The former is a genuine freedom in the Racah-Wigner algebra, a result of Schur's lemmas, but the latter is a result of a different kind of arbitrariness in the irrep matrices.

Butler (1981), Bickerstaff (1980) and Bickerstaff and Wybourne (1981) have given detailed discussions of phase freedoms of the Racah-Wigner algebra. For our purposes we divide these phase and multiplicity freedoms into coupling, branching and (continuous) orientation freedom. The coupling freedoms occur in the calculation of 6j symbols. During the 6j calculation a set of 'basis' triads emerge. All other triads are fixed relative to this basis set by choosing the phases (and magnitudes in the case of multiplicity) of 6j symbols and once all phases are chosen the rest of the symbols follow recursively. The 3jm factors are calculated after the 6js of the group and subgroup. Again, once all phase and multiplicity choices are made all other 3jms follow recursively. (Note, however, that our transformation coefficient calculations do not use 3jm factors which depend on coupling choices). A branching choice occurs for every non-primitive ket but in some cases an extra phase choice must be made - the continuous orientation choice. A complex primitive irrep in the group

or subgroup seems to be a necessary condition for the appearance of such a choice. It is not a sufficient condition however: SO_2 has a complex primitive but there is no orientation choice for $SO_3 \supset SO_2$ (see Butler 1976). Bickerstaff (1980, Bickerstaff and Wybourne 1981) has argued that when one makes such a choice one is fixing a relationship between basis triads (he calls them 'product antecedents'). For an orientation point of view we are fixing a relationship between the two primitive kets. Because of this restriction a transformation between sets of 3jm factors with different orientation choices requires non-unity primitive transformation coefficients. A continuous orientation choice occurs in the point group imbeddings $D_n \supset C_n$, $D_{odd} \supset C_2$, $T \supset C_3$ and $C_m \supset C_n$ and in continuous group imbeddings such as the $SU_6 \supset SU_2 \times SU_3$, $SU_3 \supset U_1 \times SU_2$ and $SU_3 \supset SO_3$ branchings discussed in appendix 2. The 3jms for which the choices were made were

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}_{SO_3}^{SU_3} \quad \begin{pmatrix} 1 & 1 & 1 \\ 1.1 & 1.1 & -2.0 \end{pmatrix}_{U_1 \times SU_2}^{SU_3} \quad \begin{pmatrix} 1^3 & 1^2 & 1 \\ 3.0 & 2.1^2 & 1.1 \end{pmatrix}_{SU_2 \times SU_3}^{SU_6} \tag{4.1.1}$$

For $SU_3 \supset SO_3$ the phase choice has an immediately apparent effect. If the phase of the 3jm is changed to

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}_{SO_3}^{SU_3}{}' = e^{i\theta} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}_{SO_3}^{SU_3} \tag{4.1.2}$$

then, from

$$\begin{pmatrix} 1 & 1 & 1 \\ & & \\ 1 & 1 & 1 \end{pmatrix}' = \langle 11|11\rangle'\langle 11|11\rangle'\langle 11|11\rangle' \begin{pmatrix} 1 & 1 & 1 \\ & & \\ 1 & 1 & 1 \end{pmatrix} \qquad (4.1.3)$$

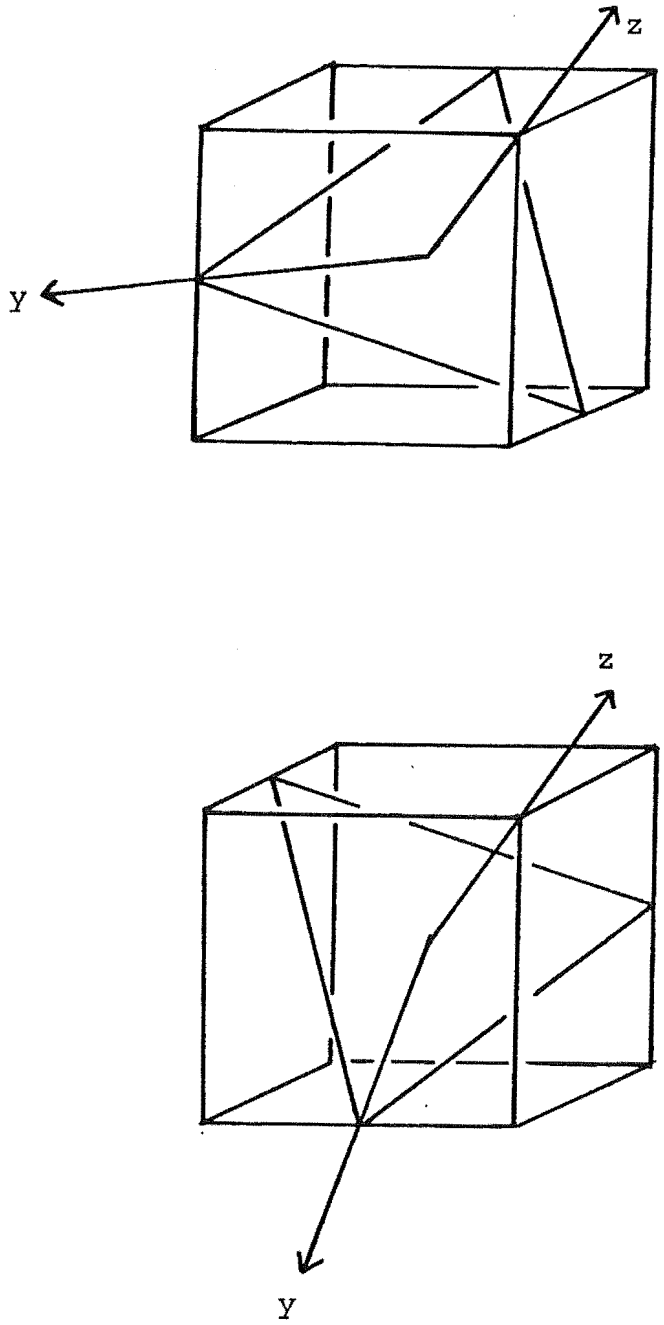
(a factorized and rearranged form of eqn. 3.2.1) one is restricted to

$$\langle 11|11\rangle' = e^{-i\theta/3} = \langle 1^2 1|1^2 1\rangle'^* \qquad (4.1.4)$$

analogous to the $D_3 \supset C_3$ example discussed in appendix 1.

The 'double root' orientation phase choices are not so well understood. In these cases there is no freedom left in the Racah-Wigner algebra but no equations which fix the 3jms. We are forced to proceed in a rather ad hoc manner: make a choice and investigate the consequences. In all cases that we know of both roots lead to a consistent set of 3jm factors. In appendix 1 we showed that the two roots in the $T \supset D_2$ calculation correspond to two orientations of a tetrahedron, $\frac{\pi}{2}$ apart. The two tetrahedra have the same 3-fold axes but, as I shall show in the next section, the character of a 3-fold rotation about xyz is different for the two tetrahedra-equivalent to switching the classes C_3 and C_3^{-1} of the character table. In figure 2 of appendix 1 we see that in one case xyz is through a vertex, and in the other case a face, of the tetrahedron. This correspondence of operations is not a general property of double root choices. For $O \supset D_3$ the two roots correspond to the two orientations of a cube about a "D_3 triangle" shown in figure (4.1.1). In this case the two sets have different four-fold axes, and therefore different irrep matrices

FIGURE 4.1.1: Orientations of $O \supset D_3$



The two orientations of the cube about a D_3 triangle are related by a $\pi/3$ rotation about the z axis. Though the cube had been drawn as fixed in the diagram it is the D_3 triangle which should be considered to be fixed since the $D_3 \supset C_3$ orientation choice fixes the two-fold axes of D_3 and the $O \supset D_3$ choice fixes the orientation of the other axes of O relative to these.

but the character tables are the same. For the point groups a double root occurs only for $T \supset D_2$, $O \supset D_3$, $K \supset T$ and $K \supset D_5$ and we know of no continuous group examples.

The double root choice is potentially more troublesome than the continuous choice because the latter is easily recognized as a freedom of the algebra whereas the former is not. The double root choice is also rather unpredictable. There are two distinct orientations of an icosahedron about a D_3 triangle (similar to $O \supset D_3$) but there is no orientation choice for the $K \supset D_3$ 3jms. During the calculation there appeared to be a double root but the 3jm was fixed by the "Wigner" equation (Butler, Haase and Wybourne 1979 eqn 18 Butler 1981 eqn 3.3.31). (Note that the equation used did not contain coupling phase information.) The $K \supset D_3$ 3jms correspond to a particular orientation of the icosahedron relative to the D_3 triangle - the orientation of the five-fold axes could be determined by the methods discussed in the next section. This orientation must have been fixed by something we have overlooked or misunderstood. More surprises are surely in store for the reader who intends to calculate 6js and 3jms for other groups.

(4.2) Characters of representations

In appendix 1 we used transformations to the JM basis of SO_3 to determine the symmetry axes of pure rotation groups. These methods can be extended to rotation-reflection groups. A rotation - reflection group is not a subgroup of SO_3 but O_3 (= $SO_3 \times C_i$). For even parity kets the

transformation to the JM basis is the same as a pure rotation scheme and the odd parity kets are simply related (see appendix 4).

Let σ_h be a reflection in the xy plane and σ_v a reflection in the xz plane. The action of these operators on a JM ket is

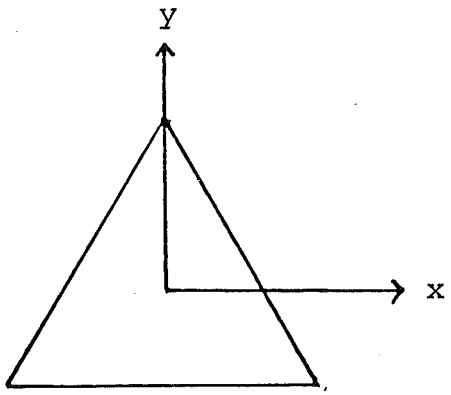
$$\sigma_h|J^{\pm}M\rangle = \pm(-)^M|J^{\pm}M\rangle \qquad (4.2.1)$$

$$\sigma_v|J^{\pm}M\rangle = \pm(-)^{J-M}|J^{\pm}-M\rangle$$

Reflections in other planes may be generated by rotating, reflecting and rotating back. For even parity kets a reflection is equivalent to a two-fold rotation about an axis perpendicular to the mirror plane. Because of this one must be careful when drawing pictures. If, for example, we make an orientation choice for $D_3 \supset C_3$ so that the y axis is a two-fold axis (appendix 1 eqn 4.11) then the D_3 operations transform the triangle in figure (4.2.1) into itself. If we consider instead $C_{3v} \supset C_3$ the xz plane is a mirror plane so C_{3v} transforms a different triangle into itself (figure 4.2.2). Note that we do not have to consider odd parity kets to determine the orientation of mirror planes.

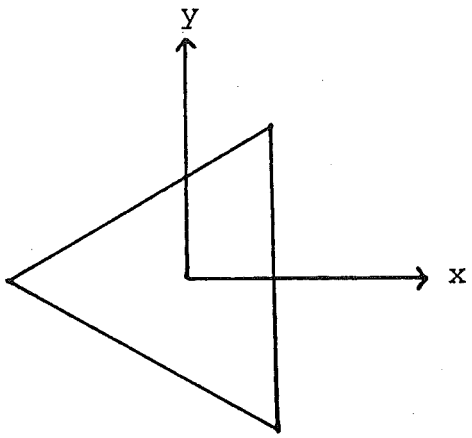
The transformation coefficients for $O_3 \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4$ to the JM basis (appendix 5) may be used to provide examples. For instance

Figure 4.2.1: Orientation of D_3



Here the y axis is a two-fold axis

Figure 4.2.2: Orientation of C_{3v}



Here the xz plane is a mirror plane

$$|2^+2^+0^+00\rangle = |2^+0\rangle(-1)$$

$$|2^-2^-0^-\tilde{0}0\rangle = |2^-0\rangle(-1) \qquad (4.2.2)$$

$$|1^+1^+\tilde{0}^+\tilde{0}0\rangle = |1^+0\rangle(+1)$$

and from (2.2.1) we have

$$\sigma_v|2^+0\rangle = +|2^+0\rangle,\ \sigma_v|2^-0\rangle = -|2^-0\rangle,\ \sigma_v|1^+0\rangle = -|1^+0\rangle \qquad (4.2.3)$$

which are the characters for 0 and $\tilde{0}$ of C_{4v} under σ_{xz} (see, for example, Koster et al. 1963, Butler 1981).

We can always determine the orientation of symmetry axes and mirror planes of a group by transforming to the JM basis. Operations such as σ_h, σ_v and rotations by π about the x,y and z axes have a simple effect on JM kets. Some operations, such as the 3-fold rotations of T in the $T \supset D_2 \supset C_2$ orientation, are more complicated. As an alternative to using the rotation matrices on JM kets we can generate a set of rotated transformation coefficients. In appendix 1 we showed that choosing a particular relationship between the primitive transformation coefficients corresponds to a rotation of the axes (appendix 1 eqn 3.3). If the two group schemes are identical then the transformation coefficients are just the matrix elements of the operation and the characters may be read directly off the table. If the group chain $SO_3 \supset SO_2$ is used the usual rotation matrices, $D^J(\alpha,\beta,\gamma)$, will be generated. Construction of matrices in this manner uses the same information as building up the matrices from the generators and 3jms of the group (Bickerstaff 1980 eqn 12.47 and p318).

TABLE 4.2.1: Transformation from $SO_3 \supset O \supset T \supset D_2 \supset C_2$ to the JM basis. The format is: $|SO_3OTD_2C_2$ ket$> = \sum_M |$JM ket$>$ x (transformation coefficient). For notation see appendix 3.

! 0 0 0 0 0 > = ! 0 0 > +1

! 1' 1' 1' 1' 1'> = ! 1' 1'> +1

! 1' 1' 1' 1'-1'> = ! 1'-1'> +1

! 1 1 1 ^0 0 > = ! 1 0 > +1

! 1 1 1 1 1 > = ! 1 1 > -1/#2 + ! 1 -1 > -1/#2

! 1 1 1 ^1 1 > = ! 1 1 > +1/#2 + ! 1 -1 > -1/#2

! 3' 3' 3' 1' 1'> = ! 3' 1'> +1/#2 + ! 3'-3'> -J/#2

! 3' 3' 3' 1'-1'> = ! 3' 3'> +J/#2 + ! 3'-1'> -1/#2

! 3' 3'-3' 1' 1'> = ! 3' 1'> +1/#2 + ! 3'-3'> +J/#2

! 3' 3'-3' 1'-1'> = ! 3' 3'> -J/#2 + ! 3'-1'> -1/#2

! 2 2 2 0 0 > = ! 2 2 > +J/2 + ! 2 0 > -1/#2 + ! 2 -2 > +J/2

! 2 2 -2 0 0 > = ! 2 2 > -J/2 + ! 2 0 > -1/#2 + ! 2 -2 > -J/2

! 2 ^1 1 ^0 0 > = ! 2 2 > -J/#2 + ! 2 -2 > +J/#2

! 2 ^1 1 1 1 > = ! 2 1 > -J/#2 + ! 2 -1 > +J/#2

! 2 ^1 1 ^1 1 > = ! 2 1 > -J/#2 + ! 2 -1 > -J/#2

! 5' 3' 3' 1' 1'> = ! 5' 5'> -J#5/2#3 + ! 5' 1'> +1/#2 + ! 5'-3'> -J/2#3

! 5' 3' 3' 1'-1'> = ! 5' 3'> -J/2#3 + ! 5'-1'> +1/#2 + ! 5'-5'> -J#5/2#3

! 5' 3'-3' 1' 1'> = ! 5' 5'> +J#5/2#3 + ! 5' 1'> +1/#2 + ! 5'-3'> +J/2#3

! 5' 3'-3' 1'-1'> = ! 5' 3'> +J/2#3 + ! 5'-1'> +1/#2 + ! 5'-5'> +J#5/2#3

! 5'^1' 1' 1' 1'> = ! 5' 5'> +J/#2.3 + ! 5'-3'> -J#5/#2.3

! 5'^1' 1' 1'-1'> = ! 5' 3'> -J#5/#2.3 + ! 5'-5'> +J/#2.3

! 3 1 1 ^0 0 > = ! 3 0 > -1

! 3 1 1 1 1 > = ! 3 3 > -#5/4 + ! 3 1 > -#3/4 + ! 3 -1 > -#3/4
+ ! 3 -3 > -#5/4

! 3 1 1 ^1 1 > = ! 3 3 > -#5/4 + ! 3 1 > +#3/4 + ! 3 -1 > -#3/4
+ ! 3 -3 > +#5/4

! 3 ^1 1 ^0 0 > = ! 3 2 > +J/#2 + ! 3 -2 > +J/#2

! 3 ^1 1 1 1 > = ! 3 3 > +J#3/4 + ! 3 1 > -J#5/4 + ! 3 -1 > -J#5/4
+ ! 3 -3 > +J#3/4

! 3 ^1 1 ^1 1 > = ! 3 3 > -J#3/4 + ! 3 1 > -J#5/4 + ! 3 -1 > +J#5/4
+ ! 3 -3 > +J#3/4

! 3 ^0 0 0 0 > = ! 3 2 > +J/#2 + ! 3 -2 > -J/#2

Table 4.2.2: Character table for T

	E	a*	b	$3C_{2z}$ $3\bar{C}_{2z}$	$\bar{E}$	$\bar{a}$	$\bar{b}$
0	1	1	1	1	1	1	1
$\frac{1}{2}$	2	1	1	0	-1	-1	-1
1	3	0	0	-1	3	0	0
$\frac{3}{2}$	2	ω^2	ω^4	0	-2	ω^5	ω
$-\frac{3}{2}$	2	ω^4	ω^2	0	-2	ω	ω^5
2	1	ω^2	ω^4	1	1	ω^5	ω
-2	1	ω^4	ω^2	1	1	ω	ω^5

$\omega = e^{-i\pi/3}$, $\omega^3 = -1$

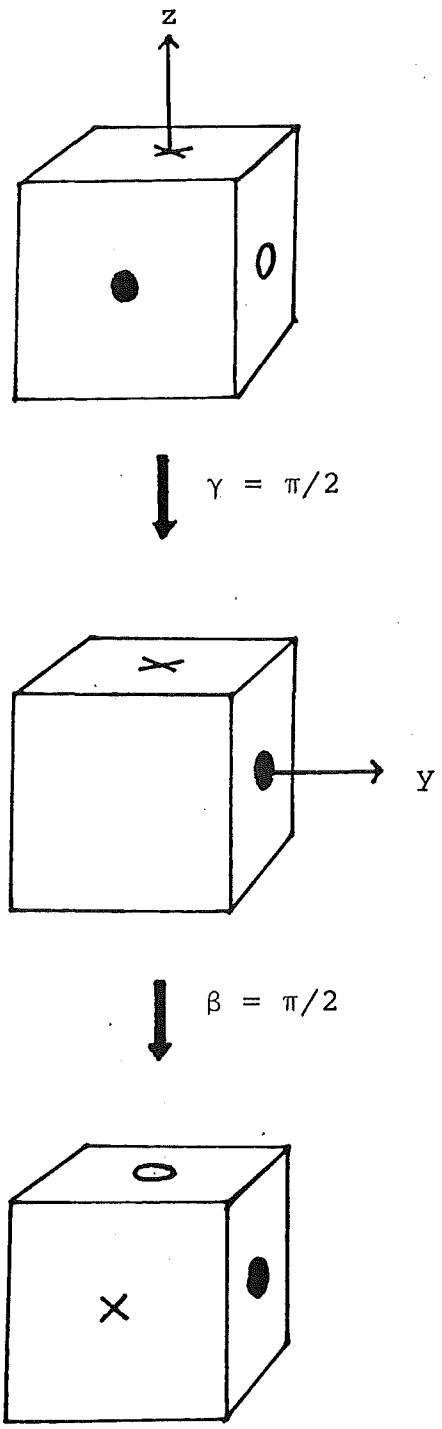
*The classes a and b are 3-fold rotations about xyz. With the +ve orientation phase choice (table 4.2.3) $a = C_3^{-1}$, $b = C_3$. With the -ve choice (table 4.2.4) $a = C_3$, $b = C_3^{-1}$.

Consider Bickerstaff's example: T in the $T \supset D_2 \supset C_2$ basis (see also appendix 1 section 5). The z axis is a two-fold axis because the lowest group is C_2, the x and y axes are also two-fold, because of the (real) choice of orientation phase for the $D_2 \supset C_2$ 3jm factors, and therefore xyz is a three-fold axis. These statements are easily verified by inspection of the transformation coefficients from $SO_3 \supset D \supset T \supset D_2 \supset C_2$ to the JM basis (table 4.2.1) Two-fold rotations about the x,y and z axes (Messiah 1961 appendix C11) yield the correct characters (table 4.2.2). A 3-fold rotation about xyz is generated by the Euler angles $\alpha = 0, \beta = \frac{\pi}{2}, \gamma = \frac{\pi}{2}$. In the active convention this means a rotation by $\gamma = \frac{\pi}{2}$ about the laboratory z axis then by $\beta = \frac{\pi}{2}$ about the laboratory y axis (figure 4.2.3) Equation (3.3) of appendix 1 gives the primitive transformation coefficients

$$A = \frac{1}{2} - \frac{i}{2}, \quad B = \frac{1}{2} - \frac{i}{2} \tag{4.2.6}$$

Table (4.2.3) was generated by transforming $T \supset D_2 \supset C_2$ into itself using this choice. The orientation phase choice (appendix 1 eqn 5.1) was +, the choice of Butler (1981). The character of $\frac{3}{2}(T)$ is $-\frac{1}{2} + i\frac{\sqrt{3}}{2}$ ($= \omega^4$ in table 4.2.2) for this case. For the -ve orientation choice (table 4.2.4) the character of $\frac{3}{2}(T)$ is $-\frac{1}{2} - i\frac{\sqrt{3}}{2}$ ($= \omega^2$). Inspection of the character table of T (table 4.2.2) shows that the orientation choice corresponds to switching the class labels for C_3 and C_3^{-1}. As discussed above this is a result of the $\frac{\pi}{2}$ difference in orientation between the two tetrahedra.

Figure 4.2.3: Euler Angles for a Rotation about xyz



A rotation about xyz is accomplished by a rotation by $\gamma = \pi/2$ about z and $\beta = \gamma/2$ about y. Since we use the active convention the axes are fixed.

TABLE 4.2.3: Rotation of $T \supset D_2 \supset C_2$. This table gives the transformation of the $T \supset D_2 \supset C_2$ basis into itself, with a rotation of $2\pi/3$ about xyz. The format is: $|T \supset D_2 \supset C_2\rangle = \Sigma\ |T \supset D_2 \supset C_2$ ket$\rangle$ x (transformation coefficient). For notation see appendix 3. The $T \supset D_2$ orientation choice (appendix 1 eqn 3.3) was positive.

```
! 0  0  0 > = ! 0  0  0 > +1
! 1' 1' 1'> = ! 1' 1' 1'> +1/2 -J/2 + ! 1' 1'-1'> +1/2 -J/2
! 1' 1'-1'> = ! 1' 1' 1'> -1/2 -J/2 + ! 1' 1'-1'> +1/2 +J/2
! 1 ^0  0 > = ! 1 ^1  1 > -1
! 1  1  1 > = ! 1 ^0  0 > +J
! 1 ^1  1 > = ! 1  1  1 > +J
! 3' 1' 1'> = ! 3' 1' 1'> -1/4 +#3/4 +J/4 +J#3/4
             + ! 3' 1'-1'> -1/4 +#3/4 +J/4 +J#3/4
! 3' 1'-1'> = ! 3' 1' 1'> +1/4 +#3/4 +J/4 -J#3/4
             + ! 3' 1'-1'> -1/4 -#3/4 -J/4 +J#3/4
!-3' 1' 1'> = !-3' 1' 1'> -1/4 -#3/4 +J/4 -J#3/4
             + !-3' 1'-1'> -1/4 -#3/4 +J/4 -J#3/4
!-3' 1'-1'> = !-3' 1' 1'> +1/4 -#3/4 +J/4 +J#3/4
             + !-3' 1'-1'> -1/4 +#3/4 -J/4 -J#3/4
! 2  0  0 > = ! 2  0  0 > -1/2 +J#3/2
!-2  0  0 > = !-2  0  0 > -1/2 -J#3/2
```

TABLE 4.2.4: Rotation of $T \supset D_2 \supset C_2$. This table is the same as table 4.2.3 except that the $T \supset D_2$ orientation choice was negative.

```
! 0  0  0 > = ! 0  0  0 > +1
! 1' 1' 1'> = ! 1' 1' 1'> +1/2 -J/2 + ! 1' 1'-1'> +1/2 -J/2
! 1' 1'-1'> = ! 1' 1' 1'> -1/2 -J/2 + ! 1' 1'-1'> +1/2 +J/2
! 1 ^0  0 > = ! 1 ^1  1 > -1
! 1  1  1 > = ! 1 ^0  0 > +J
! 1 ^1  1 > = ! 1  1  1 > +J
! 3' 1' 1'> = ! 3' 1' 1'> -1/4 -#3/4 +J/4 -J#3/4
             + ! 3' 1'-1'> -1/4 -#3/4 +J/4 -J#3/4
! 3' 1'-1'> = ! 3' 1' 1'> +1/4 -#3/4 +J/4 +J#3/4
             + ! 3' 1'-1'> -1/4 +#3/4 -J/4 -J#3/4
!-3' 1' 1'> = !-3' 1' 1'> -1/4 +#3/4 +J/4 +J#3/4
             + !-3' 1'-1'> -1/4 +#3/4 +J/4 +J#3/4
!-3' 1'-1'> = !-3' 1' 1'> +1/4 +#3/4 +J/4 -J#3/4
             + !-3' 1'-1'> -1/4 -#3/4 -J/4 +J#3/4
! 2  0  0 > = ! 2  0  0 > -1/2 -J#3/2
!-2  0  0 > = !-2  0  0 > -1/2 +J#3/2
```

Note that a rotation which is not a member of the group is not allowed - the transformation coefficients will become un-normalized. If a scheme which includes SO_3 is used then any rotation is allowed but some will mix the point group irreps. In the $T \supset D_2 \supset C_2$ examples a 3-fold rotation about xyz is not an element of D_2 or C_2 and the operation has mixed the D_2 and C_2 irreps.

Similar procedures were used to check the character tables of Butler (1981) for other groups. Butler (1981 chapter 5) uses the techniques described here to discuss the relationship between the axes of different subgroups of the octahedral group. The $O \supset D_4 \supset C_4$ basis, for example, is related to the $O \supset D_3 \supset C_3$ basis by the Euler angles $\alpha = -\frac{\pi}{4}$, $\beta = -\cos^{-1}\left(\frac{1}{\sqrt{3}}\right)$, $\gamma = 0$. The primitive transformation coefficients are therefore

$$OD_3C_3\,{}^{<\frac{1}{2}\frac{1}{2}\frac{1}{2}|\,\frac{1}{2}\frac{1}{2}\frac{1}{2}>}OD_4C_4 = \frac{\sqrt{2} + 2i - i\sqrt{2}}{(8.3-4.3\sqrt{2}-8\sqrt{3}+4\sqrt{2.3})^{\frac{1}{2}}}$$

$$OD_3C_3\,{}^{<\frac{1}{2}\frac{1}{2}-\frac{1}{2}|\,\frac{1}{2}\frac{1}{2}\frac{1}{2}>}OD_4C_4 = \frac{1-\sqrt{3}+i-i\sqrt{2}-i\sqrt{3}+i\sqrt{2.3}}{(8.3-4.3\sqrt{2}-8\sqrt{3}+4\sqrt{2.3})^{\frac{1}{2}}}$$

The full table appears in Butler (1981).

This lengthy discussion of axes and bases may appear to have removed the main advantage of the building up method - that one needs only character theory results. This is not the case. The calculations are still done using only equations which arise from the Racah-Wigner algebra and the present discussion merely demonstrates that

we can always deduce the basis information that is necessary for a particular application. Indeed, many calculations need no information about the basis. The crystal field energy level calculations discussed in chapter 5 and the multiquark hadron dissociation calculations discussed in chapter 3 (see Black and Wybourne 1981) require only a consistent choice of 3jms and 6js. Other calculations require a small amount of information, such as the transformation properties of the parallel and perpendicular magnetic field operators (Chapter 5) or electric dipole operators (chapter 6). These properties are easily deduced from transformation coefficients and are given in the character tables of Butler (1981).

CHAPTER 5

CRYSTAL FIELD AND SUPERPOSITION MODEL CALCULATIONS FOR Re^{3+} IONS IN CaF_2

The study of Re^{3+} ions in CaF_2 and SrF_2 is complicated by the existence of several different sites, corresponding to various charge compensation mechanisms, and the averaging effect of the various possible orientations of the sites, which destroys polarization information. In the absence of checks on the eigenstates, such as Zeeman experiments (Freeth and Jones 1981), a crystal field fit to a set of energy levels does not guarantee correct interpretation of data. Indeed, a survey by Baker (Hayes 1974) noted inconsistencies between the crystal field parameters for various Re^{3+} ions at tetragonal sites. Recent experimental work by Edgar et al. (1979) (on Er^{3+}) and Freeth and Jones (1981) (on Ce^{3+}, Nd^{3+} and Er^{3+}) has removed some of these anomalies but the large variations of the parameters for other ions in the series may be contrasted with other hosts, such as $LaCl_3$ (Dieke 1968, table 16).

In this chapter I shall reconsider the parameterization of the tetragonal crystal field and re-calculate its eigenstates and energy levels. The commonly used parameters B_0^2, B_0^4, B_4^4, B_0^6 and B_4^6 give little indication that the tetragonal sites are approximately cubic (O_h symmetry), with an interstitial F^- reducing the symmetry to C_{4v}. Our Hamiltonian consists of O_h and C_{4v} scalars and makes the symmetries more obvious. The standard approach is to perform a calculation in the JM ($SO_3 \supset SO_2$) basis and then assign point group irreps to

the eigenvectors. We use the Wigner-Eckart theorem in the point group basis, avoiding the use of the JM basis entirely. Not only are the basis states irreps of the site symmetry (here C_{4v}) but they are also close to being eigenstates of the entire crystal field Hamiltonian and so are more physical than JM basis states.

Crystal field parameters are a summary of the interactions of a host crystal with a rare earth ion. The superposition model (Newman 1971) has been used to relate these parameters to the enviroment of the ion for several hosts. I shall use the crystal field parameters to deduce the distortions of the tetragonal sites.

(5.1) Crystal-field and Zeeman Calculations

Russell-Saunders (SLJ) coupling is appropriate for rare-earth ions so the group chain $O_3^S \times O_3^L \supset O_3^J \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4$ is used in our calculations. The crystal field Hamiltonian is written as a sum of tensor operators which transform as S = 0, L = J = 2^+, 4^+ or 6^+ and as the identity irrep (0) of the site symmetry group. The five C_{4v} scalars are given in the JM basis in table (5.1.1). The two which are both O_h and C_{4v} scalars are widely used for octahedral symmetry with four-fold x,y and z axes (Hutchings 1964), but the C_{4v} scalars are new. The difference between ours and most other conventions is that all our C_{4v} scalars have known O_h symmetry. Hempel (1976) and some of the authors in Donini (1979) use similar conventions.

Table 5.1.1: Transformation from $O_3 \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4$ to the JM basis

$$|1^+1^+\tilde{0}^+\tilde{0}0> = + |1^+0>$$
$$|1^+1^+1^+11> = - |1^+1>$$
$$|1^+1^+1^+1-1> = - |1^+-1>$$

$$|2^+2^+0^+00> = - |2^+0>$$

$$|4^+0^+0^+00> = + \sqrt{5}/2\sqrt{6}(|4^+0> + \sqrt{5/14}(|4^+4> + |4^+-4>))$$
$$|4^+2^+0^+00> = + \sqrt{5}/2\sqrt{3}(|4^+0> - \sqrt{7/10}(|4^+4> + |4^+-4>))$$

$$|6^+0^+0^+00> = - 1/2\sqrt{2}(|6^+0> - \sqrt{7/2}(|6^+4> + |6^+-4>)$$
$$|6^+2^+0^+00> = + \sqrt{7}/2\sqrt{2}(|6^+0> + \sqrt{2}/2\sqrt{7}(|6^+4> + |6^+-4>$$

The labels in the kets on the left are irreps of O_3, O_h, D_{4h}, C_{4v} and C_4. The complete table is given in appendix 5. Note that the orientation phase choices are such that x,y and z are 4-fold axes of O_h and z is a four-fold axis of C_{4v} (see appendix 1). For notation see appendix 3.

We write the crystal-field Hamiltonian as

$$H_{cf} = X^{2^+2^+0^+00}\ \sqrt{5}\ U^{2^+2^+0^+00} + X^{4^+0^+0^+00}\ \sqrt{9}\ U^{4^+0^+0^+00} + X^{4^+2^+0^+00}\ \sqrt{9}\ U^{4^+2^+0^+00} + X^{6^+0^+0^+00}\ \sqrt{13}\ U^{6^+2^+0^+00} + X^{6^+2^+0^+00}\ \sqrt{13}\ U^{6^+2^+0^+00} \qquad (5.1.1)$$

where the labels refer to O_3, O_h, D_{4h}, C_{4v} and C_4 respectively. The unit tensors U^k have been multiplied by $\sqrt{|k|}$ (following Judd 1963) to make the $X^{k\lambda}$ ($\equiv X^{k^+\lambda^+0^+00}$) approximately equal to the splittings they produce. The O_3 reduced matrix elements of the U^k are given by Nielson and Koster (1963).

In the JM basis the tetragonal Hamiltonian is often written in terms of spherical tensors C^k_q as

$$H_{cf} = B^2_0C^2_0 + B^4_0C^4_0 + B^4_4C^4_4 + B^6_0C^6_0 + B^6_4C^6_4 \qquad (5.1.2)$$

This gives little indication of the relative importance of the O_h and C_{4v} distortions. The parameterization used by Edgar et al (1979) and Freeth and Jones (1981) distinguishes an axial part

$$H_{axial} = B^2_0C^2_0 + B^4_0C^4_0 + C^6_0C^6_0 \qquad (5.1.3)$$

from an octahedral part

$$H_{oct} = B^4(C^4_0 + \frac{\sqrt{5}}{\sqrt{14}}(C^4_4 + C^4_{-4}) + B^6(C^6_0 - \frac{\sqrt{7}}{\sqrt{2}}(C^6_4 + C^6_{-4})) \qquad (5.1.4)$$

This is preferable to (5.1.2) but C^4_0 and C^6_0 do not have well-defined transformation properties under O_h and are not orthogonal to the terms in equation (5.1.4). The $X^{k\lambda}$ are related to the B^k_q via table 5.1.1 and the relationships

$$U^2 = -7.2/\sqrt{3.5.7}\ C^2$$

$$U^4 = +7\sqrt{2}/\sqrt{7.11}\ C^4 \qquad (5.1.5)$$

$$U^6 = -\ 7.2.5/\sqrt{3.7.11.13}\ C^6$$

(See Wybourne 1965 equation 2.37).

The Zeeman Hamiltonian is

$$H_{Zeeman} = \beta\mathcal{H}(g_s\underline{S} + \underline{L}) \qquad (5.1.6)$$

$\beta$is the Bohr magneton, $\mathcal{H}$ the magnetic field and g_s (= 2.00232) is the g value of a free electron. $\underline{S}$ and $\underline{L}$ transform as $1^+(O_3)$ and have O_3 reduced matrix elements

$$\langle L_1\|\underline{L}\|L_2\rangle = \delta_{L_1L_2}[L(L+1)(2L+1)]^{\frac{1}{2}} \qquad (5.1.7)$$

The expression for x,y,z in the JM basis

$$|10\rangle = z$$

$$|1\pm1\rangle = \mp\frac{1}{\sqrt{2}}(x \pm iy) \qquad (5.1.8)$$

taken with table 5.1.1 shows that $H_z(H_\parallel)$ transforms as $|1^+1^+\tilde{0}^+\tilde{0}0\rangle$ and $H_x(H_\perp)$ as $\frac{1}{\sqrt{2}}(|1^+1^+1^+11\rangle - |1^+1^+1^+1\text{-}1\rangle)$. The g values $g_\parallel$ and $g_\perp$ are determined by the relationship

$$g = \frac{\Delta E}{\beta\mathcal{H}} \qquad (5.1.9)$$

where ΔE is the energy separation when the magnetic field $\mathcal{H}$ is applied. It is usual, and physically justified, to multiply the matrix elements of $\underline{L}$ by an orbital reduction factor k, which is treated as an extra parameter when fitting g-values (see, for example, Bleany 1964, Hayes 1974).

I calculated the matrix elements of the crystal field, Zeeman and spin-orbit (see Wybourne 1965) operators

with a computer program which used Butler's (1981) point group tables and the Wigner-Eckart theorem equations discussed in section 2.2. The basis states are approximate eigenstates of the crystal field Hamiltonian so the process of the matching up the theoretical energies to experimental data is simplified. Once an approximate set of parameters was found a least-squares program was used to improve the fit.

I diagonalized the complete matrix for the ground term of each ion to allow for crystal field mixing of the J multiplets (J mixing). Intermediate coupling (Wybourne 1965), which improves the accuracy of the calculations by allowing for the admixture of other terms by the spin-orbit interaction, was used for Nd^{3+} and Er^{3+}. The largest change in any parameter caused by the inclusion of intermediate coupling was 9% for X^{22} of $Nd^{3+}:CaF_2$. For Yb^{3+} and Ce^{3+} there is no intermediate coupling correction, since there is only one term, while for the rest of the series there is either insufficient data to obtain a unique set of parameters or a conflict that cannot be resolved by adding intermediate coupling (see section 5.4).

Crystal field parameters are often published with no indication of uncertainties. The numerical uncertainties may be calculated by a least-squares routine (see, for example, Bevington 1969) or by simply varying the parameters to determine their limits, as was done by Baker and Blake (1970). Errors also arise from ignoring many electron effects (Newman 1971, Judd 1977) but these contributions are not

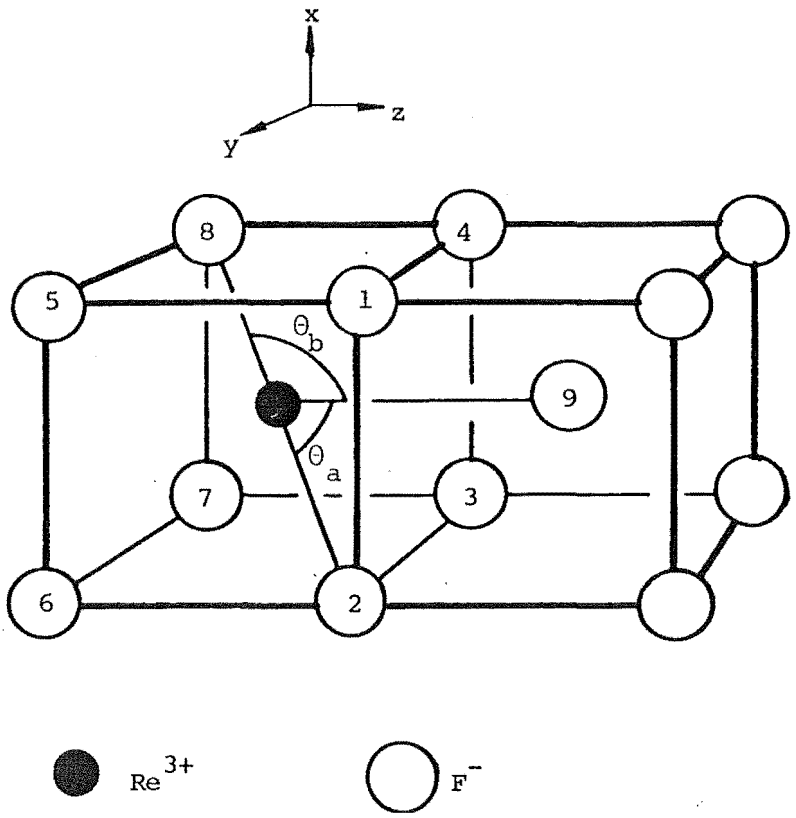
expected to produce large changes in the parameters and are certainly not the largest source of error in my superposition calculations.

(5.2) Superposition model calculations

The superposition model makes no assumptions about the interaction mechanisms between the rare earth ion and its neighbours except that the effects of the individual ligands are independant and therefore have axial ($C_{\infty v}$) symmetry. Newman (1971) has shown that the crystal-field parameters may be written as functions of the co-ordinates (R,θ,Φ) of the surrounding ions and strictly positive 'intrinsic parameters', $\bar{A}_n$, for these ions. The first shell of surrounding ions is responsible for most of the crystal field so our calculations include the eight nearest neighbours and the interstitial. These are labelled 1-9 in figure (5.2.1). The Re^{3+} ion is at the origin and the interstitial is on the z axis. The angular co-ordinates of the nearest neighbours are $(\theta_a, \frac{\pi}{4} + n\frac{\pi}{2})$ for n = 1-4 and $(\theta_b, \frac{\pi}{4} + n\frac{\pi}{2})$ for n = 5-8.

Direct information about the distortions of the tetragonal sites appears to be limited to the endor data of Baker et al. (1968) for Ce^{3+} and Yb^{3+} in CaF_2 and Kiro and Low (1971) for Ce^{3+} and Nd^{3+} in CaF_2 with F^- and H^- charge compensation. Though interpretation is complicated by covalency effects Kiro and Low indicate that for Ce^{3+} sites the distance from Ce^{3+} to ions 1-8 is the undistorted distance $\sqrt{3}\ a_o$ where a_o (= 1.36 Å) is one quarter of the lattice constant. The F^- interstitial repels ions 1-4 and attracts the Ce^{3+} ion,

Figure 5.2.1: Model of the tetragonal CaF_2 site



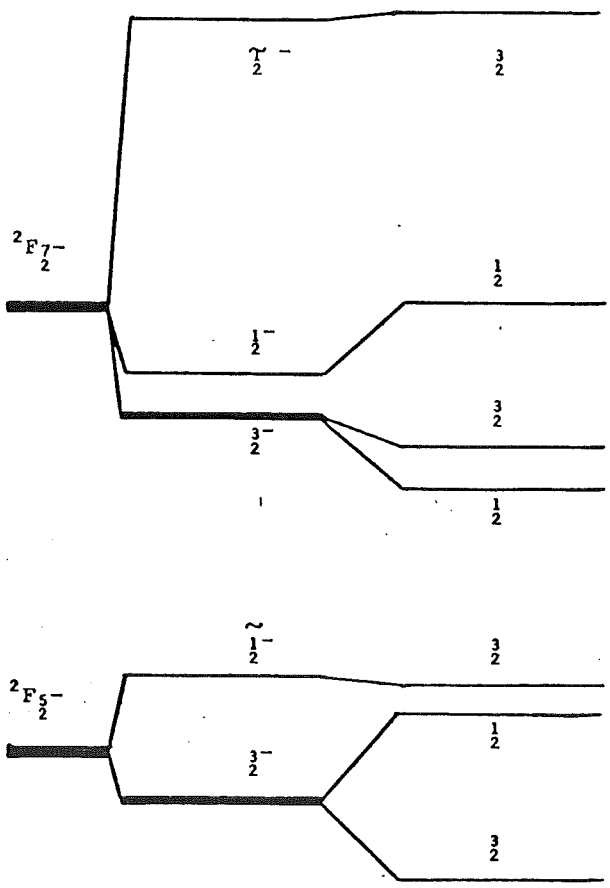
decreasing the distance to $a_o(2-\delta)$ where $\delta = .13$. Ions 5-8 move with the Ce^{3+}. Thus Θ_a increases from the cubic value 54.7° to 63° and Θ_b somewhat less, from 125.3° to 129°. An H^- interstitial produces a slightly larger distortion.

Newman (1978) has shown that for rare earth ions in cubic sites in CaF_2, SrF_2 and BaF_2 the intrinsic parameters $\bar{A}_4$ and $\bar{A}_6$ follow a power law $\left(\frac{R_o}{R}\right)^{t_n}$, where $t_4=6.3\pm1.4$ and $t_6=10.1\pm1.1$. These power laws, the distances discussed above, and the ratios X^{42}/X^{40} and X^{62}/X^{60} give just enough information to use the superposition model to calculate Θ_a and Θ_b. $\bar{A}_4$ and $\bar{A}_6$ are then calculated using $R_o = \sqrt{3}\, a_o$, the distance to the nearest neighbours. Calculations involving second-order parameters are likely to be unreliable, because the (mainly electrostatic) effects of ions other than the nine we consider will be appreciable (Newman 1971), but we shall draw some qualitative conclusions.

(5.3) Tetragonal Ce^{3+} sites in CaF_2

To illustrate our methods we shall consider the example of Ce^{3+} in detail. Freeth and Jones (1981) obtained an excellent fit to their data for this ion. Their results contradict some of the data reported by Manthey (1973). I have calculated point-group parameters using their data and Baker et al's (1959) epr measurements (figure 5.3.1). The basis states are approximate eigenstates of the Hamiltonian: for all cases except the two $\frac{7}{2}^-(O_3)\frac{1}{2}(C_{4v})$ doublets the square of the largest eigenvector is greater than 0.9 so the

Figure 5.3.1: Energy levels of $Ce^{3+}:CaF_2$



	Energy (cm^{-1})		Square of the largest eigenvector
	Experimental*	Calculated	
	3562±2	3562	0.91
	2824±3	2824	0.55
	2305±2	2305	0.99
	2191±1.3	2191	0.56
	577±2	577	0.90
	-	516	0.99
	0	0	1.00

Parameters (cm^{-1})

$\zeta = 619\pm1$ $X^{40} = -1025\pm3$ $X^{42} = 404\pm3$ $X^{22} = 554\pm5$

$X^{60} = 1129\pm6$ $X^{62} = 213\pm10$

g-values

	experimental†	calculated
$g_{\parallel}$	3.038 ± .003	3.038
$g_{\perp}$	1.396 ± .002	1.396

$k = 0.9807$*

* Freeth and Jones (1981)

† Baker et al (1959)

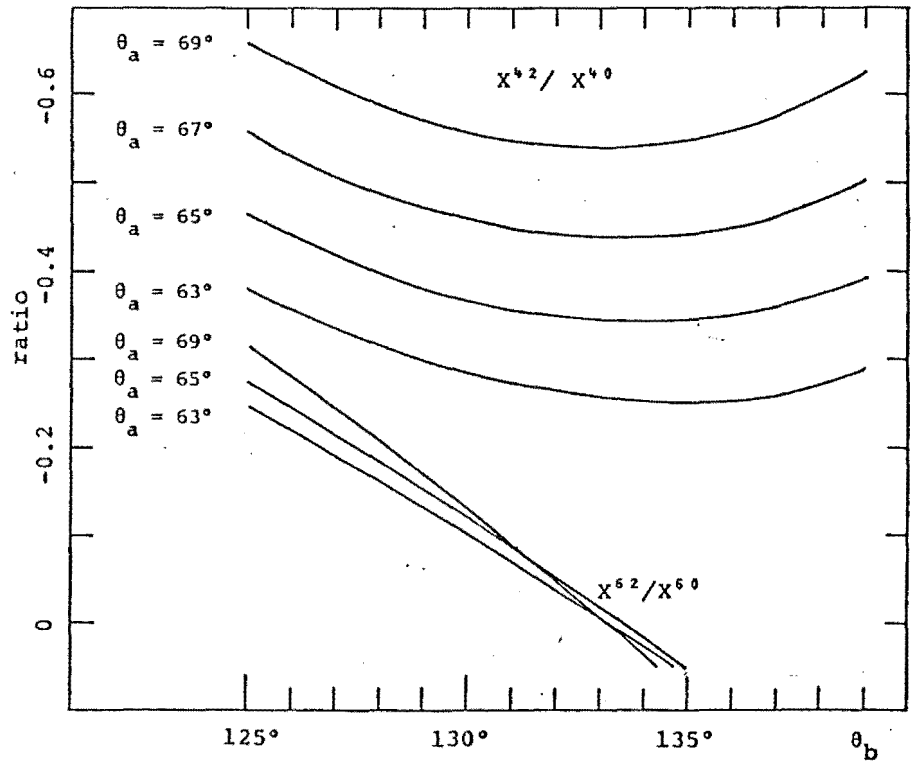
assignment of irreps is unambiguous. The diagram illustrates the descent of symmetry approach and the insight provided by our parameters: the free ion SLJ states are perturbed by an O_h field and then an appreciably smaller C_{4v} field.

The first excited state has not been observed but its placement at 516 cm^{-1} rather than the 110 cm^{-1} calculated by Manthey (1973) improves Mims (1976) calculation of the electric field effect for $Ce^{3+}:CaF_2$. Mim's parameter B_{15} in his table 6.6 is reduced by a factor of five, making it only twice the experimental value rather than ten times. Arkhipov and Malkin 1980) reached similar conclusions by re-calculating the energy levels, using Manthey's data.

My superposition calculations suggest that the addition of an F^- interstitial to a cubic site causes changes in X^{40} and X^{60} as well as X^{22}, X^{42} and X^{62}, the ratio X^{40}/X^{60} decreases by about 30% when the effects of the interstitial (including distortions) are included. This is compounded by a decrease in $\bar{A}_4/\bar{A}_6$ (see section 5.5). The O_h levels shown in figure 2 are therefore not those expected for Ce^{3+} in cubic CaF_2 sites but rather the effect of the O_h part of the total crystal field. It has sometimes been assumed that the addition of an interstitial to a cubic site requires the crystal field to be modified simply by superimposing an axial term (equation 5.1.3) on the cubic Hamiltonian. This argument ignores not only the changes in the intrinsic parameters but also the nearest neighbour distortions. The effects of these distortions are large enough to allow us to calculate the co-ordination angles.

To illustrate the calculation I have graphed X^{42}/X^{40} and X^{62}/X^{60} against θ_b for various values of θ_a

Figure 5.3.2: Superposition-model parameter ratios for $Ce^{3+}:CaF_2$



$\delta = 0.13, \quad t_4 = 6.3, \quad t_6 = 10.1$

(figure 5.3.2). The experimental values $X^{42}/X^{40} = .395 \pm .005$ and $X^{62}/X^{60} = .19 \pm .01$ give $\theta_a = 65° \pm 2°$ and $\theta_b = 128° \pm 2°$. Decreasing the power laws, increasing δ or increasing the distance from the Ce^{3+} to ions 5-8 (see figure 5.2.1) increases the magnitude of these ratios, giving a smaller θ_a and a larger θ_b. Kiro and Low deduced the angles $\theta_a = 63° \pm 1°$ and $\theta_b = 129° \pm 1°$ from their endor measurements. The two calculations of the angles are independent. Not only was the endor determination of δ completely separate from the calculation of θ_a and θ_b but also the effect being measured, the coupling of the Ce^{3+} electrons to F^- nuclei, is different from the crystal-field effects used in my analysis.

The interstitial gives a positive contribution to X^{22} and the distortion of the nearest neighbours a negative one. This has been noted by Baker (Hayes 1974 table 6.2). Suppose $\bar{A}_2$ follows a power law $\left(\frac{R_o}{R}\right)^{t_2}$. With the angles reported by Kiro and Low t_2 must be less than 10 for X^{22} to be positive. With the angles calculated above t_2 must be less than 5. Newman (1980) has argued that t_2 should be about 5.5 so the experimental result that X^{22} is positive suggests that my calculations have overestimated θ_b and underestimated θ_a. With Kiro and Low's angles the superposition model predicts the correct signs for all the crystal field parameters.

(5.4) Crystal field parameters for Re^{3+} ions in CaF_2 and SrF_2

In addition to their work in Ce^{3+} Freeth and Jones (1981) obtained parameters for Nd^{3+} in CaF_2 and SrF_2 and Er^{3+} in CaF_2 (see also Edgar et al (1979). Their studies included Zeeman experiments and they showed that the transverse Zeeman effect (Judd and Runciman 1976) can identify the C_{4v} irreps

Table 5.4.1: Crystal field parameters for Re^{3+} ions (cm^{-1})

	X^{22}	X^{40}	X^{42}	X^{60}	X^{62}
$Ce^{3+}:CaF_2(F^-)$*	554 ± 5	-1025 ± 3	404 ± 3	1129 ± 6	-213 ± 10
$Nd^{3+}:CaF_2(F^-)$*	533 ± 6	- 780 ± 4	332 ± 6	840 ± 3	-249 ± 3
$Nd^{3+}:SrF_2(F^-)$*	389 ± 6	- 738 ± 6	296 ± 6	713 ± 3	-204 ± 3
$Er^{3+}:CaF_2(F^-)$*	372 ± 6	- 577 ± 4	238 ± 6	506 ± 3	-153 ± 3
$Er^{3+}:CaF_2(H^-)$†	486 ± 10	- 238 ± 6	249 ± 8	374 ± 5	-192 ± 5
$Yb^{3+}:CaF_2(F^-)$§	231 ± 30	- 336 ± 50	178 ± 30	524 ± 80	- 87 ± 13

*Freeth and Jones (1981)

†Edgar et al (1979)

§Baker and Blake (1970)

of the energy levels for ions with an odd number of electrons. Baker and Blake (1970) have used a combination of endor, epr and optical data to derive parameters for Yb^{3+} in CaF_2 and Edgar et al (1979) have calculated parameters for Er^{3+} in CaF_2 with H^- charge compensation. I have transformed the JM basis parameters obtained by these authors into point group basis parameters (table 5.4.1) and checked their interpretations against my own calculations. These parameters all have the same signs and, apart from $Er^{3+}:CaF_2(H^-)$, similar ratios.

Some of the parameters (obtained from various authors) for the rest of the series are very different from these. In figures (5.4.1-8) I have summarized the data and graphed some of the low lying energy levels for Pr^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+} and Tm^{3+} against increasing C_{4v} perturbation:

$$H_{C_{4v}} = X_{C_{4v}} (\sqrt{5}\, U^{2}{}^{+}2^{+}0^{+}00 + 0.67\sqrt{9}\, U^{4}{}^{+}2^{+}0^{+}00 - 0.43\sqrt{13}\, U^{6}{}^{+}2^{+}0^{+}00) \qquad (5.4.1)$$

which is added to

$$H_{O_h} = X^{4}{}^{+}0^{+}0^{+}00\ \sqrt{9}\, U^{4}{}^{+}0^{+}0^{+}00 + X^{6}{}^{+}0^{+}0^{+}00\ \sqrt{13}\, U^{6}{}^{+}0^{+}0^{+}00 \qquad (5.4.2)$$

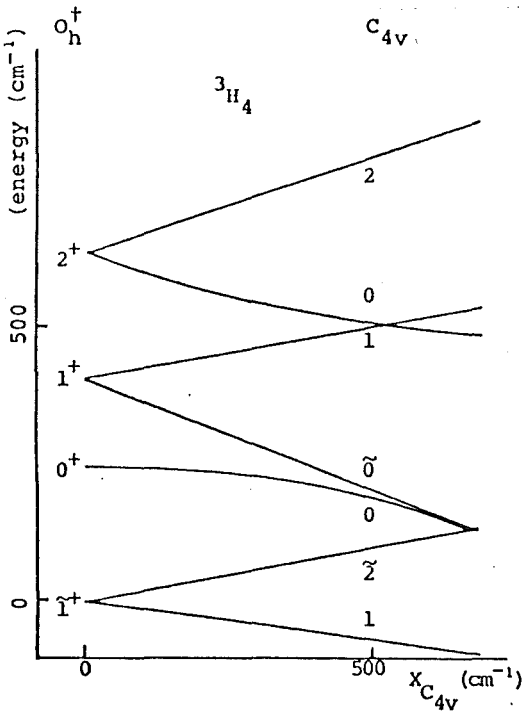
The numerical factors in (5.4.1) were obtained by averaging the $CaF_2(F^-)$ parameters (table 5.4.1). X^{40}, X^{60} and a likely value for $X_{C_{4v}}$ were determined by interpolation. I expect the experimental values to be close to these. For several ions

the limited data available is in accord with my calculations. For others there is some conflict but in most of these cases the information from various sources is contradictory and it is not certain that all the data originate from tetragonal F^- sites.

Experimental techniques such as those used by Freeth and Jones (1981) could remove some of these conflicts. For ions with an even number of electrons the Zeeman effect does not give as much information as for the odd-electron ions studied by them because only one (the irrep 1) of the five true (that is, non-spinor) irreps of C_{4v} is a doublet. Nevertheless, in the presence of a magnetic field the selective laser excitation techniques which these authors have extended, following Tallant and Wright (1975), Kliava et al. (1978), could be used to excite only one of the magnetically inequivalent sites. The fluorescence would then be polarized and therefore give more information.

Note that because the O_h levels shown on the diagrams are not those expected for cubic sites (see sections 5.3 and 5.5) the lowest O_h levels for Dy^{3+} (figure 5.4.6) are not in the order deduced by Bierig and Weber (1963). I have ignored Gd^{3+} because a discussion of the second-order effects which become important when the first-order crystal field vanishes is outside the scope of this work (see Wybourne 1965 and Baker's article in Hayes 1974).

Figure 5.4.1: Energy levels of $Pr^{4+}(f^2)$



Estimated parameters (cm^{-1})

$X^{40} = -900 \quad X^{60} = 1000 \quad X_{C_{4v}} = 540$

$g_{\|} = 3.92$ $(k = 0.9815)$

Experimental data

epr: Wetsel et al. (1969), Lupei et al. (1979) } $g_{\|} = 3.86$

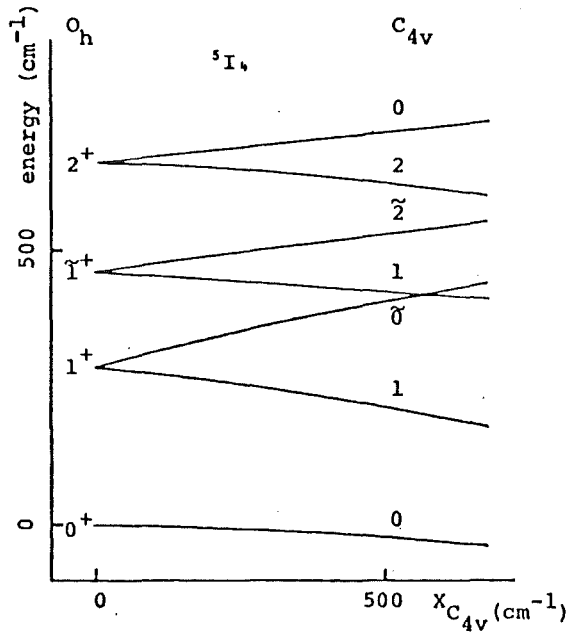
Note: we have changed their $g_{\|}$ to our definition.

Optical: Hargreaves (1972) His splittings are too small by a factor of 3 and he has a singlet ground-state.

Kliava (1979) Observed several sites with selective laser excitation.

†See text

Figure 5.4.2: Energy levels of $Pm^{3+}(f^4)$

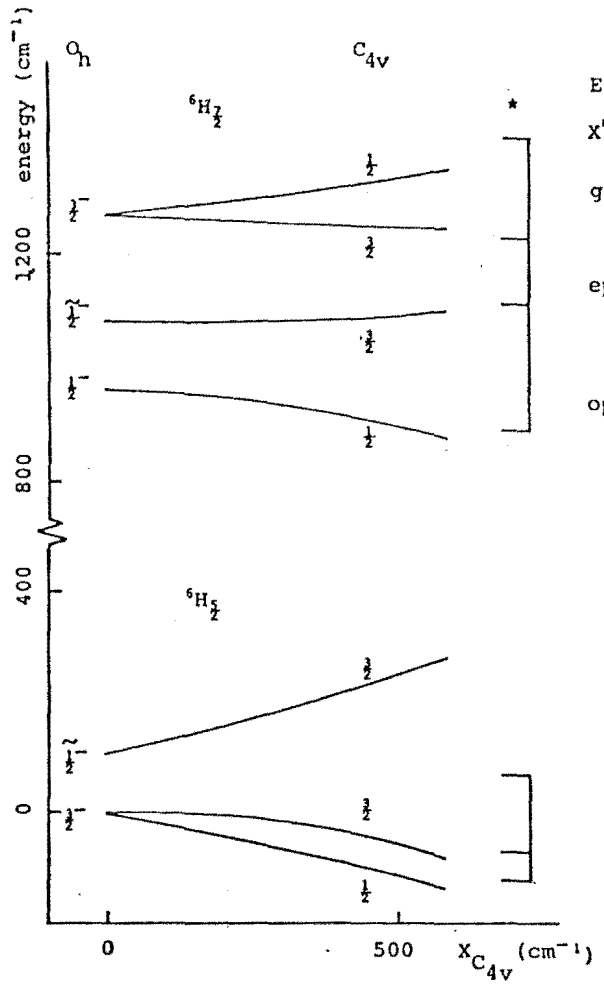


Estimated parameters (cm^{-1})

$X^{40} = -750 \quad X^{60} = 800 \quad X_{C_{4v}} = 510$

singlet ground state

Figure 5.4.3: Energy levels of $Sm^{3+}(f^5)$



Estimated parameters (cm^{-1})

$X^{40} = -700$ $X^{60} = 750$ $X_{C_{4v}} = 490$

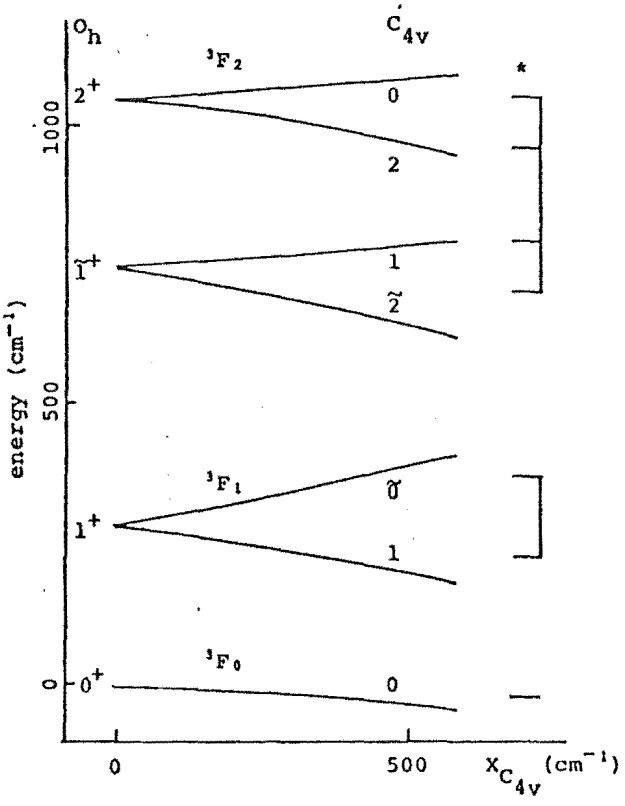
$g_{\|} = 0.01$ $g_{\perp} = 0.78$ ($k = 0.9835$)

Experimental data

epr: Antipin et al. (1965), Evans and McLaughlan (1966), Newman and Woodward (1974) } $g_{\|} < .006$, $g_{\perp} = 0.823$

optical: *Rabbiner (1967) Fitting these levels (and higher levels, not shown) gave wrong g-values and anomalous parameters.

Figure 5.4.4: Energy levels of $Eu^{3+}(f^6)$



Estimated parameters (cm^{-1})

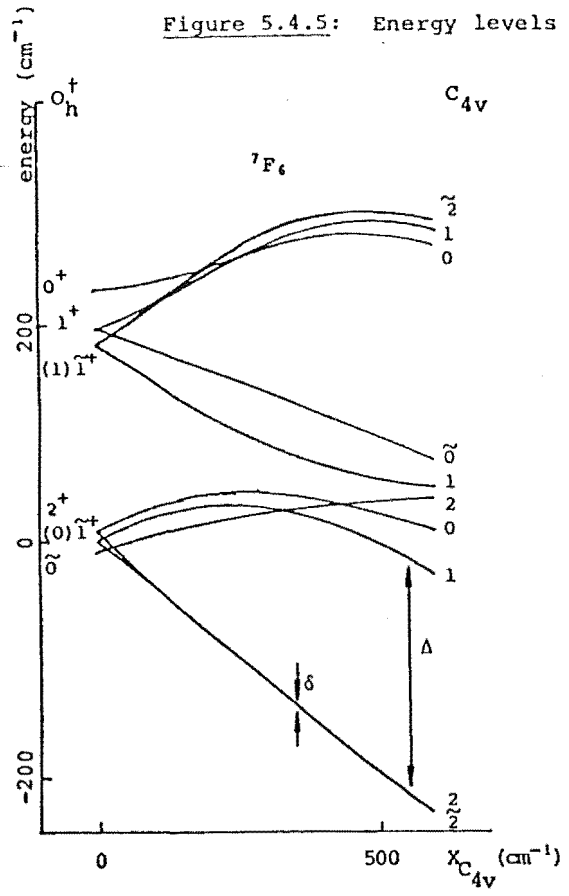
$X^{40} = -660$ $X^{60} = 690$ $X_{C_{4v}} = 470$

singlet ground state

Experimental data

Optical: *Bokii et al (1968) Data only determines X^{22}, X^{40} and X^{42}. The energy levels can be fitted but since the data was presented only in diagrammatic form accurate parameters cannot be determined.

Figure 5.4.5: Energy levels of $Tb^{3+}(f^8)$



Estimated parameters

$X^{40} = -630$ $X^{60} = 640$ $X_{C_{4v}} = 430$

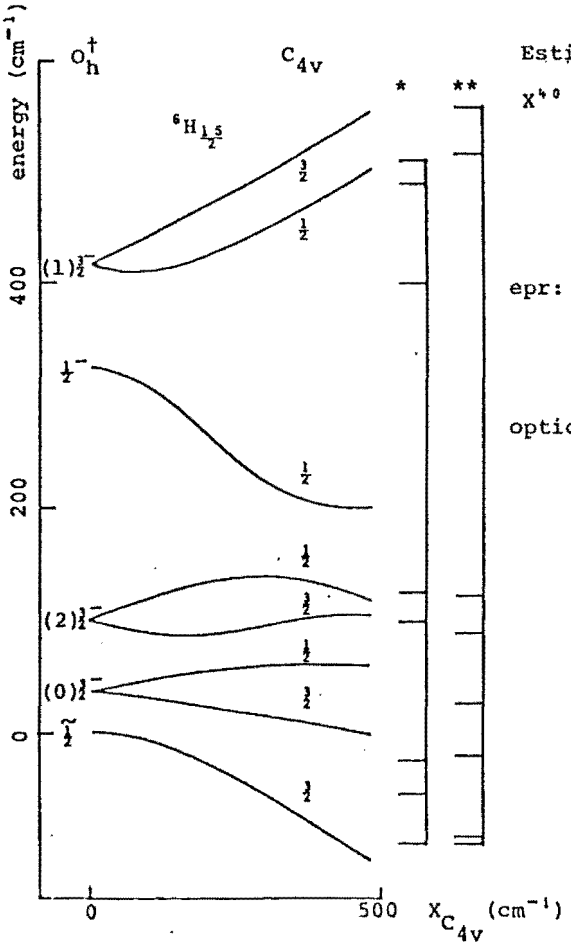
$g_\parallel = 17.9$ (k = 0.9858)

Experimental data

epr: Antipin et al. (1968) (for SrF_2)
$\Delta = 123\ cm^{-1}$ $\delta = 0.48\ cm^{-1}$ $g_\parallel = 17.95$
Note: the parameters quoted by Antipin et al. are not uniquely determined and are different from ours.

†The labels in parenthesis are branching multiplicity labels for $O_3 \supset O_h$.

Figure 5.4.6: Energy levels of $Dy^{3+}(f^9)$



Estimated parameters (cm^{-1})

$X^{40} = -625$ $X^{60} = 585$ $X_{C_{4v}} = 410$

$g_\parallel = 17.1$ $g_\perp = 0.002$ (k = 0.9865)

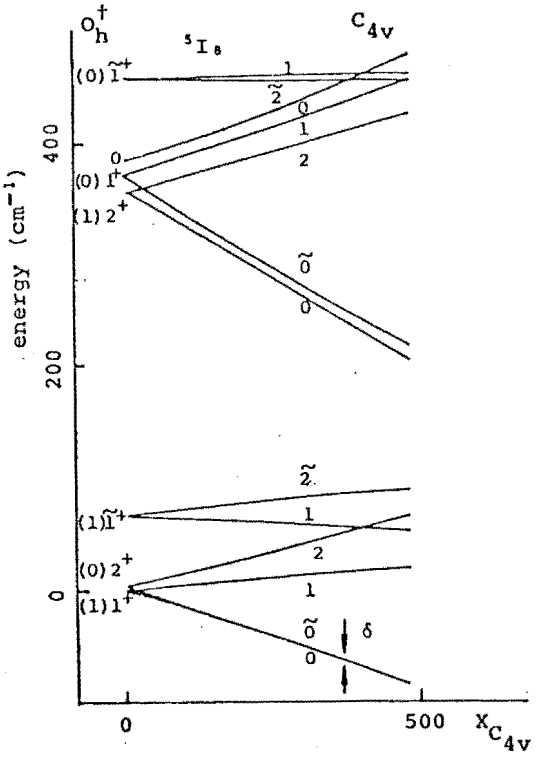
Experimental data

epr: Bierig and Weber (1963) $g_\parallel = 1.7$
$g_\perp = 2.82$
Antipin et al. (1973) disagreed, saw no resonance.

optical: *Nara and Schlesinger (1972)
**{Luks et al. (1969), Antipin et al. (1973)
Sivaram et al. (1979)
There is a disagreement on the assignment of energy levels to sites (also higher levels, not shown). Both sets require anomalous parameters and g-values different from Bierig and Webers. We found no choice of parameters which reproduced these g-values.

†see text and figure 5.4.5

Figure 5.4.7: Energy levels of $Ho^{3+}(f^{10})$



Estimated parameters (cm^{-1})

$X^{40} = -620$ $X^{60} = 530$ $X_{C_{4v}} = 390$

$g_\parallel = 14.9$ ($k = 0.987$)

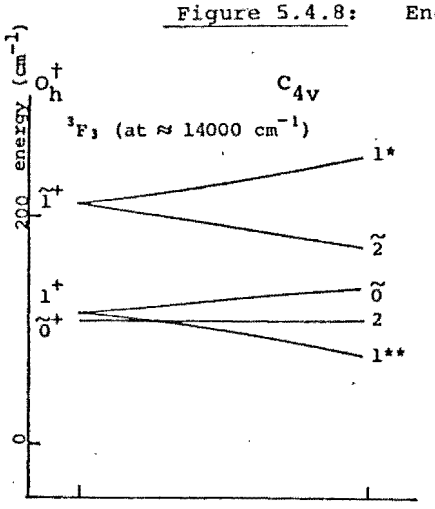
Experimental data

epr: Kornienko and Rybaltovskii (1972)
$\delta = 0.033\ cm^{-1}$, $g_\parallel = 14.8$

optical: Lal and Ramachandra Rao (1978)
Seelbinder and Wright (1979)
Not enough data to construct energy-level scheme.

†see figure 5.4.5

Figure 5.4.8: Energy levels of $Tm^{3+}(f^{12})$



Estimated parameters (cm^{-1})

$X^{40} = -530$ $X^{60} = 500$ $X_{C_{4v}} = 300$

singlet ground-state

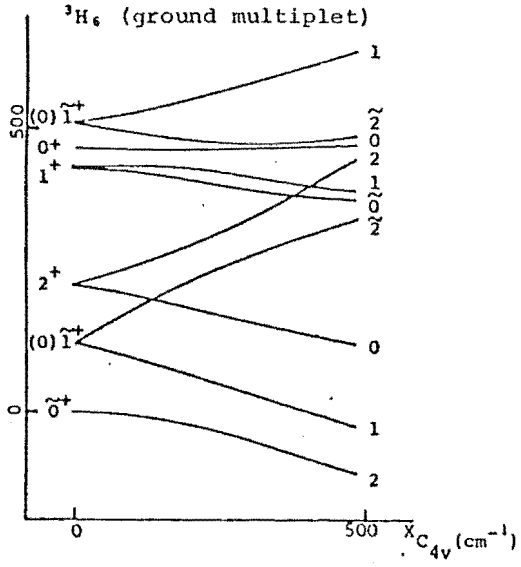
* $g_\parallel = 1.1$ ** $g_\parallel = 5.4$ ($k = 0.9888$)

Experimental data

epr: Hayes and Twidell (1961) No resonance for Tm^{3+}.

optical: Muto (1973). Zeeman experiments confirm singlet ground state but suggest that the $^3F_3$ doublets $\tilde{1}^+(O_h)$ $1(C_{4v})$ and $1^+(O_h)$ $1(C_{4v})$ are in reverse order to our diagram.

† see figure 5.4.5



(5.5) Superposition model calculations for Re^{3+} ions in CaF_2 and SrF_2

My calculations of Θ_a, Θ_b, $\bar{A}_4$ and A_6 (table 5.5.1) and the endor determinations of δ suggest that the distortions for Nd^{3+} and Er^{3+} $CaF_2(F^-)$ sites are smaller than those for Ce^{3+} or Yb^{3+}. A simple hard-sphere model shows that Nd^{3+} and Er^{3+} ions cause less distortion because their sizes are closer to that of Ca^{2+}. The larger Ce^{3+} ions stretch the lattice and the smaller Yb^{3+} ions are free to move towards the interstitial. Reduced force constants for ions smaller than Ca^{2+} are suggested by the infra-red experiments of Hayes et al. (1973), (see also Hayes 1974 section 2.5). For Nd^{3+} and Er^{3+} Θ_b, derived from the superposition model, is less than the cubic value of 125.3°. It seems unlikely that this is the case and I noted in section 5.3 that several assumptions could be modified to increase this angle.

The F^- interstitial should produce less distortion in the larger SrF_2 lattice. Since δ has not been measured for Nd^{3+}:$SrF_2(F^-)$ my conclusion that Θ_a decreases is tentative.

I used the same power laws for both F^- and H^- ions in my calculation of the $\bar{A}_n$ of the nearest neighbour F^- and the interstitial H^- for Er^{3+}:$CaF_2(H^-)$. The corresponding angles Θ_a, Θ_b were estimated from those derived for the Er^{3+}:$CaF_2(F^-)$ site and the difference between the angles for the Ce^{3+}:$CaF_2(F^-)$ and Ce^{3+}:$CaF_2(H^-)$ sites reported by Kiro and Low (1971). The ratio $\bar{A}_n(H^-)/\bar{A}_n(F^-)$ is 3 for n = 4 and 6, which is consistent with the large polarizability of the H^- ion (see Jones 1979 for a survey of the properties of H^- sites). Because of the cancellation effects of the nearest neighbour and interstitial contributions to X^{22} (see section 5.3)

Table 5.5.1: Co-ordination angles and intrinsic parameters for Re^{3+} ions

	δ	θ_a	θ_b	$\bar{A}_4(cm^{-1})$	$\bar{A}_6(cm^{-1})$
$Ce^{3+}:CaF_2(F^-)$	$.13 \pm .06^{\dagger\ddagger}$	$65° \pm 2°$	$128° \pm 2°$	103 ± 5	47 ± 3
$Nd^{3+}:CaF_2(F^-)$	$.08^{\dagger} \pm .04$	$63.5° \pm 2°$	$123° \pm 2°$	75 ± 5	34 ± 4
$Nd^{3+}:SrF_2(F^-)$	$.08 \pm .06^*$	$63° \pm 2°$	$123° \pm 2°$	70 ± 5	28 ± 4
$Er^{3+}:CaF_2(F^-)$	$1.0 \pm .08^*$	$63° \pm 2°$	$123° \pm 2°$	56 ± 3	20 ± 3
$Er^{3+}:CaF_2(H^-)$	$.12 \pm .08^*$	$65° \pm 3°^*$	$123° \pm 3°^*$	$F^-: 33 \pm 3$ $H^-: 100 \pm 10$	14 ± 2 49 ± 4
$Yb^{3+}:CaF_2(F^-)$	$.13 \pm .06^{\ddagger}$	$68° \pm 4°$	$128° \pm 3°$	36 ± 5	25 ± 4

†Kiro and Low (1971)

‡Baker et al. (1968)

*Estimated

it is impossible to obtain a reliable estimate of the ratio $\bar{A}_2(H^-)/\bar{A}_2(F^-)$.

Comparison between Er^{3+}:$CaF_2(H^-)$ and Er^{3+}:$CaF_2(F^-)$ shows that $\bar{A}_6(F^-)$ and $\bar{A}_4(F^-)/\bar{A}_6(F^-)$ are smaller for the H^- site. $A_4(F^-)/\bar{A}_6(F^-)$ is, on average, 40% larger for cubic CaF_2 sites (Stedman and Newman 1971b, Newman 1978) than for our tetragonal sites and 20% smaller for LaF_3 sites (Stedman and Newman 1971a), which have C_2 symmetry and nine nearest neighbours. These trends appear to be a breakdown of the superposition approximation, possibly caused by a change in covalent bonding effects. They must not be confused with the superposition-model prediction that X^{40}/X^{60} is smaller for the tetragonal sites than the cubic ones. As a result of these two effects the crystal field for an ion at a cubic site is different from the O_h part of the field at a tetragonal site.

(5.6) Conclusions

I have shown that the superposition model may be used to analyse the distortions of charge compensated impurity sites. The example of tetragonal CaF_2 sites gave systematic trends along the Re^{3+} series and gave similar results to endor experiments for the co-ordination angles of Ce^{3+}. The differences in the ratio $\bar{A}_4(F^-)/\bar{A}_6(F^-)$ between cubic (no interstitial), tetragonal (F^- interstitial) and tetragonal (H^- interstitial) sites is presumed to be a breakdown of the superposition approximation.

For all ions for which unambiguous data is available the parameters X^{22}, X^{42} and X^{60} are positive and X^{40} and X^{62}

are negative. The superposition model requires these signs. I predict that the parameters for the other ions have the same signs and that the energy level schemes are similar to figures 5.4.1 - 5.4.8.

Calculations in the appropriate point group basis have the advantage of using good quantum numbers for both the states and the crystal field parameters. This symmeterization gives more physical insight. The basis states are close to being eigenstates of the Hamiltonian and the descent in symmetry from O_h to C_{4v} is evident in the parameters.

CHAPTER 6

INTENSITY CALCULATIONS

The description of electric dipole transitions of rare earth ions formulated by Judd (1962) and Ofelt (1962) has been a useful starting point in the analysis of experimental intensity data. Like the crystal field parameters discussed in chapter 5 the intensity parameters can absorb various effects not specifically anticipated by the theory. Judd (1962) showed that his high temperature parameters (T_2, T_4, T_6) could account for all possible mechanisms and Newman and Balasubramanian (1975) have discussed the generality of the low temperature parameterization.

At "high" temperatures (room temperature and above) smeared out transitions between J-multiplets are observed. The intensity of most of these transitions is quite insensitive to the environment but some transitions, the ones which follow electric quadrupole selection rules, are very sensitive and have been termed 'hypersensitive' by Jorgenson and Judd (1964). Various authors (e.g. Judd 1966, 1979, 1980, Carnall et al 1964, Gruen and De Kock 1966, Mason et al 1975, Henrie et al 1966, Peacock 1975, Malta and deSa 1980) have discussed these transitions. More information is needed to clearly distinguish the mechanisms which have been proposed. Experiments at low temperatures, where transitions between sharp crystal field levels are

observed, give a much richer set of parameters than high temperature experiments. Unfortunately quantitative low temperature intensity measurements are also more difficult so less experimental data is available.

In chapter 5 the use of a point group basis lead to more natural parameters and basis states than the standard JM basis. The same advantages apply to intensity calculations - the parameters and selection rules arise more naturally. In this chapter I shall discuss the low temperature parameterization. High temperature parameters have all basis information summed out so the point group approach is no advantage, though the results may be recovered directly. Intensity calculations for Er^{3+} in CaF_2 are performed by way of example.

(6.1) JUDD-OFELT THEORY IN A POINT GROUP BASIS

The Judd-Ofelt electric dipole transition mechanism involves the odd parity crystal field, written in a point group basis as

$$H_{odd} = \sum_{\substack{k=1,3,5,7 \\ a}} A^{k\bar{}a00} \, D^{k\bar{}a00} \qquad (6.1.1)$$

where

$$D^{k\bar{}00} = \sum_j r_j^k \, C^{ka00}(\theta_j,\phi_j)$$

The a are branching multiplicity labels (usually irrep labels of intermediate groups), necessary to distinguish the occurences of the identity irrep of the site symmetry group G. The C^{ka00} are point group basis versions of the spherical

tensors (C^k_q) discussed in chapter 5. This parameterization is used because radial integrals will appear explicitly in later equations. In chapter 5 we absorbed these integrals into the crystal field parameters. Note that this Hamiltonian, plus the even crystal field Hamiltonian (eqn 5.1.1) includes all one-electron effects (Newman 1971).

The electric dipole operator transforms as $1^-(O_3)$ and is represented by the operator $D^{1^-}b\rho i$, where ρ is an irrep of G, b a multiplicity label and i a basis label. The polarization of the electric vector corresponding to each $b\rho i$ is determined by the transformation of the point group basis to the JM basis and expression in terms of x,y and z (eqn 5.1.8).

The Judd-Ofelt method is well documented so only the results will be quoted. The oscillator strength of a spectral line corresponding to a transition from a component λ to a component δ is proportional to $|\langle\lambda|D^{1^-}b\rho i|\delta\rangle|^2$. The total intensity is a sum of these terms over the components of the states, and the polarizations. For f^n-f^n transitions the matrix elements are zero in first order but second order matrix elements involving the odd crystal field and the opposite-parity (to f^n) configurations $f^{n-1}d$ and $f^{n-1}g$ are non-zero. Judd (1962) and Ofelt (1962) simplified these matrix elements by a closure over the opposite-parity states. In a point group basis equation (13) of Judd (1962) becomes :

$$\langle \alpha J d \mu \ell | D^{1^- b \rho i} | \alpha' J' d' \mu' \ell' \rangle$$

$$= \sum_{\substack{a,t=1,3,5,7 \\ \lambda=2,4,6}} |\lambda| A^{t^- a00} \Xi(t,\lambda) \sum_c \begin{pmatrix} \lambda^+ \\ c \\ \rho \\ i \end{pmatrix} \begin{pmatrix} 1^- & \lambda^+ & t^- \\ b & c^* & a \\ \rho & \rho^* & 0 \\ i & i^* & 0 \end{pmatrix} \qquad (6.1.2)$$

$$\times \langle \alpha J d \mu \ell | U^{\lambda^+ c \rho i} | \alpha' J' d' \mu' \ell' \rangle$$

where

$$\Xi(t,\lambda) = 2 \sum_{n'\ell'} |\ell||\ell'| (-)^{\ell+\ell'} \qquad (6.1.3)$$

$$\begin{Bmatrix} 1 & \lambda & t \\ \ell & \ell' & \ell \end{Bmatrix} \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & t & \ell \\ 0 & 0 & 0 \end{pmatrix} \langle n\ell | r | n'\ell' \rangle \langle n\ell | r^t | n'\ell' \rangle / \Delta(n'\ell')$$

Where $\Delta(n'\ell') = E(n\ell) - E(n'\ell')$ is the (negative) difference in energy between the f^n configuration and the opposite parity configuration. This energy difference is assumed to be the same for the initial and final states.

The products $A^{t^- a00} \Xi(t,\lambda)$ may be used as free parameters. For each $\lambda = 2,4,6$ we have one parameter $A^{t^- a00} \Xi(t,\lambda)$ for each time the identity irrep of G is contained in $t^- = (\lambda \pm 1)^-$.

In practice the initial and final states are not pure basis states, since these are mixed by the spin-orbit interaction and the crystal field. Accurate calculations therefore require the eigenfunctions of the (even parity) crystal field.

(6.2) Parameterization Schemes

Newman and Balasubramanian (1975) have discussed the generality of the low temperature parameterization. They argue that all static one-electron effects may be represented by a vector field. In our notation the components of the vector field are written

$$\underline{V} = \sum_{b\rho} V_{b\rho} = \sum_{\lambda=2,4,6} X^{\lambda^+ b\rho} |\lambda|^{\frac{1}{2}} \sum_i U^{\lambda^+ b\rho i} \qquad (6.2.1)$$

where the ρ are, as above, the irreps of G contained in $1^-(O_3)$ (we are using the same normalization as for the crystal field parameters in chapter 5). Note that Newman and Balasubramanian use the symbols σ and π to mean parallel and perpendicular to the z axis respectively, the opposite to Wybourne (1965). Equation (6.1.2) contains matrix elements of the operators in (6.2.1) but (6.2.1) contains more parameters.

To clarify the connection with the Judd-Ofelt formalism a different parameterization is used. A vector field may be expressed as a sum of vector spherical harmonics (Edmonds 1960). Using point group 3jms, instead of JM basis 3jms we can write point group vector tensors (using unit tensor normalization)

$$\underline{U}^{k^\pm}_{J^\mp c\nu\ell} = \sum_{\substack{a\mu j \\ b\rho i}} U^{k^\pm a\mu j}\, \underline{e}_{1^- b\rho i}\, |J|^{\frac{1}{2}} \begin{pmatrix} J^\mp \\ c \\ \nu \\ \ell \end{pmatrix} \begin{pmatrix} k^\pm & 1^- & J^\mp \\ a & b & c^* \\ \mu & \rho & \nu^* \\ j & i & \ell^* \end{pmatrix} \qquad (6.2.2)$$

where the $\pm$ sign goes with even/odd k. Like the crystal field

the static vector field must be scalar under G:

$$\underline{V} = \sum_{kJc} X^{k^{\pm}}_{J^{\mp}c00} |k|^{\frac{1}{2}} \sum_{ab\rho i} U^{k^{\pm}a\rho^* i^*} \underline{e}_{1^- b\rho i} |J|^{\frac{1}{2}} \begin{pmatrix} J^{\mp} \\ c \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} k^{\pm} & 1^- & J^{\mp} \\ a & b & c^* \\ \rho^* & \rho & 0 \\ i^* & i & 0 \end{pmatrix} \tag{6.2.3}$$

A component of this is

$$V_{b\rho i} = \underline{e}_{1^- b\rho i} \cdot \underline{V}$$

$$= \sum_{kJc} X^{k^{\pm}}_{J^{\mp}c00} |k|^{\frac{1}{2}} \sum_{a} U^{k^{\pm}a\rho^* i^*} |J|^{\frac{1}{2}} \begin{pmatrix} J^{\mp} \\ c \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} k^{\pm} & 1^- & J^{\mp} \\ a & b & c^* \\ \rho^* & \rho & 0 \\ i^* & i & 0 \end{pmatrix} \tag{6.2.4}$$

k must be even so that the tensor operator U^k is even parity and matrix elements within the f^n configuration do not vanish. The number of parameters is therefore the number of $A^{k^+}_{J^- c00}$ for k = 2,4,6 and J = k,k $\pm$ 1 (Note that Newman and Balasubramanian say that J must have even parity but obviously used J^- to obtain their table 2).

There are just as many $X^{k^+}_{J^- c00}$ as there are $X^{\lambda^+ b\rho}$ in eqn (6.2.1). This is a general result because (6.2.1) and (6.2.3) are both general parameterizations. (Newman and Balasubramanian give several examples). With this parameterization we see that the $X^{k^+}_{J^- c00}$ with J = k $\pm$ 1 correspond to the Judd-Ofelt parameters $A^{t^- a00}$ Ξ (t,λ) but the parameters

X^{k+}_{k-c00} are not included in the Judd-Ofelt formalism. Newman and Balasubramanian (1975) argue that because there are no such terms for $C_{\infty v}$ symmetry they vanish under the superposition approximation and so may be ignored. J = k (or rather λ = t) terms could appear in (6.1.2) if there were odd parity crystal field terms transforming as J even. These crystal field terms would also disappear under the superposition approximation and Newman (1971) has argued that odd parity terms transform only as J odd. Thus the parameterization with $X^{k+}_{(k\pm1)-c00}$ should be adequate for static effects and at low temperatures "static" transitions can be distinguished from those involving vibrations.

Krupke and Gruber (1965) and Becker (1971) found that they could not explain their phenonenologically determined $A^{\lambda a00}\ \Xi(t,\lambda)$ in terms of calculated radial integers and crystal-field parameters. In fact ratios of the form $A^{\lambda a00}\ \Xi(\lambda,\lambda+1)/A^{\lambda a00}\ \Xi(\lambda,\lambda-1)$ had the wrong sign. Newman and Balasubramanian (1975) suggest that the integrals should be extended over ligand orbitals. They also suggest the use of the superposition model. As in the case of crystal field parameters the superposition model allows one to distinguish 'intrinsic parameters' from the angular effects and one may then concentrate on constructing models, such as the overlap model (Newman 1971), to explain the intrinsic parameters.

Dagenais et al (1981) have used the results of two-photon absorption experiments to argue that Judd's high temperature parameters T_2, T_4, T_6 are inadequate. The

discrepancies were presumed to be caused by a variation in the radial integrals between the f^n multiplets and opposite parity configurations. Our parameters will have similar problems. Judd (1977) has argued that crystal field effects for different multiplets are different because the radial integrals are different. The crystal field parameters used in chapter 5 and the intensity parameters used here assume that they are constant. However, the crystal field parameterization has been quite successful so the vector field parameters should be a useful starting point.

Dynamic effects have been discussed by various authors (e.g. Faulkner and Richardson 1978, Judd 1980). Dynamic effects allow f^n-f^n electric dipole transitions even for systems with inversion symmetry because the dynamic crystal field effects (unlike the static effects for a site with inversion symmetry) can have odd parity terms.

(6.3) Selection Rules

The origin of electric dipole selection rules is very obvious from our point group basis equations. The most general parameterization of electric dipole transitions involves matrix elements of the form

$$\langle \alpha J b \lambda \ell | U^{k+} a \rho i | \alpha J' b' \lambda' \ell' \rangle \qquad (6.3.1)$$

which is non-zero only if

$$\lambda' \times \rho \supset \lambda \qquad (6.3.2)$$

where ρ is the polarization of the electric vector. For magnetic dipole transitions the matrix elements

$$\langle \alpha J \lambda \ell | U^{1^+ a \rho i} | \alpha' J' b' \lambda' \ell' \rangle \qquad (6.3.3)$$

give the selection rule

$$\lambda' \times \rho \supset \lambda \qquad (6.3.4)$$

where ρ is now the polarization of the magnetic vector. Restrictions on S,L and J are also evident in the matrix elements, but these selection rules are often broken by spin-orbit and crystal field mixing.

(6.4) Re^{3+} ions in CaF_2

The C_{4v} symmetry of the F^- charge compensated sites (see chapter 5) allows for 9 parameters for $J = k \pm 1$:

$$X^{2^+}_{1^-1^-\tilde{0}^-00} \qquad X^{2^+}_{3^-1^-\tilde{0}^-00}$$

$$X^{4^+}_{3^-1^-\tilde{0}^-00} \qquad X^{4^+}_{5^-(0)1^-\tilde{0}^-00} \qquad X^{4^+}_{5^-(1)1^-\tilde{0}^-00} \qquad (6.4.1)$$

$$X^{6^+}_{5^-(0)1^-\tilde{0}^-00} \qquad X^{6^+}_{5^-(1)1^-\tilde{0}^-00}$$

$$X^{6^+}_{7^-(0)1^-\tilde{0}^-00} \qquad X^{6^+}_{7^-(1)1^-\tilde{0}^-00}$$

(The numbers in parenthesis are branching multiplicity labels).

The transformation coefficients (appendix 5) give

$$|1^-1^-\tilde{0}^-00\rangle = - |1^-0\rangle$$

$$|1^-1^-1^-11\rangle = + |1^-1\rangle \qquad (6.4.2)$$

$$|1^-1^-1^-1\text{-}1\rangle = - |1^--1\rangle$$

So the operators appearing in equation 6.2.4 for the electric vector parallel to the z axis are:

$$U^{2^+2^+0^+00} \qquad U^{4^+0^+0^+00} \qquad U^{4^+2^+0^+00}$$

$$U^{6^+0^+0^+00} \qquad U^{6^+2^+0^+00} \qquad (6.4.3)$$

and for $\underline{E} \perp z$

$$U^{2^+\tilde{1}^+1^+11} \qquad U^{2^+\tilde{1}^+1^+1\text{-}1}$$

$$U^{4^+1^+1^+11} \qquad U^{4^+1^+1^+1\text{-}1} \qquad U^{4^+\tilde{1}^+1^+11} \qquad U^{4^+\tilde{1}^+1^+1\text{-}1}$$

$$U^{6^+1^+1^+11} \qquad U^{6^+1^+1^+1\text{-}1} \qquad U^{6^+(0)\tilde{1}^+1^+11} \qquad U^{6^+(0)\tilde{1}^+1^+1\text{-}1}$$

$$U^{6^+(1)\tilde{1}^+1^+11} \qquad U^{6^+(1)\tilde{1}^+1^+1\text{-}1} \qquad (6.4.4)$$

Judd (1966) predicted that the hypersensitive transitions should be strong for site symmetries which allowed parameters with J = 1, these being presumed to dominate. This is not

born out by the parameters of Porcher and Caro (1978,1980) for Eu^{3+} in C_{4v} sites in KY_3F_{10}, where (in our notation) $X^{2+}_{3-1-\tilde{0}-00}$ rather than $X^{2+}_{1-1-\tilde{0}-00}$ dominates the hypersensitive transitions. Quantitative information which would allow the determination of these parameters for Re^{3+}:CaF_2 C_{4v} sites does not seem to be available. As noted in chapter 5 the existence of several sites causes experimental difficulties and the averaging effect of the different orientations of the sites destroys polarization information. Careful crystal field analyses must be made to identify the energy levels before intensity calculations can be contemplated. Edgar et al (1979), Freeth (1980) and Freeth and Jones (1981) have studied Er^{3+} in detail and the energy-level structure is well understood. Unfortunately none of the intensity data given by Freeth (1980) gives information about the k = 2 parameters.

Freeth (1980) has measured relative intensities for the fluorescence of Er^{3+} from the lowest $^4S_{3/2}$ doublet to the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets. The averaging effect of the various orientations of the sites makes this fluorescence unpolarized. Since $\Delta J = 6$ for these transitions the only parameters we need to consider are $X^{6+}_{5-(0)1-\tilde{0}-00}$, $X^{6+}_{5-(1)1-\tilde{0}-00}$, $X^{6+}_{7-(0)1-\tilde{0}-00}$ and $X^{6+}_{7-(1)1-\tilde{0}-00}$. I fitted the intensity data by varying these parameters (see table 6.4.1). Inspection of the matrix elements leads one to the conclusion that all four parameters must have the same sign. These parameters were then used to calculate the intensities expected when a magnetic field is applied (table 6.4.2). In this case polarized fluorescence was

Table 6.4.1: Fluorescence from $^4S_{3/2}$ (all polarizations) Fluorescence from E_1 (lowest $^4S_{3/2}$ doublet) to $Z(^4I_{15/2})$ and $Y(^4I_{13/2})$ multiplets. The intensities for $E_1 \rightarrow Z$ and $E_1 \rightarrow Y$ cannot be compared. The energy level scheme is given by Edgar et al (1979, table 3) and Freeth (1980 table 4.19).

Final state	Theoretical Intensity	Experimental Intensity (Freeth 1980)
Z_1	0.14	laser line
Z_2	1.0	1.0 ± .2
Z_3	0.43	0.4 ± .1
Z_4	0.0059	not observed
Z_5	2.26	2.3 ± .5
Z_6	1.18	<0.4*
Z_7	0.80	0.6 ± .2
Z_8	8×10^{-7}	not observed
Y_1	1.0	1.0 ± .4
Y_2	0.33	0.2 ± .1
Y_3	0.52	0.3 ± .1
Y_4	0.20	0.7 ± .2*
Y_5	0.91	
Y_6	0.035	very small
Y_7	0.45	< .2*

Parameters: $X^{6^+}_{5^-(0)1^-\tilde{0}^-00} = 1^*$ $X^{6^+}_{5^-(1)1^-\tilde{0}^-00} = 1.12 \pm .1$

$X^{6^+}_{7^-(0)1^-\tilde{0}^-00} = 1.49 \pm .1$ $X^{6^+}_{7^-(1)1^-\tilde{0}^-00} = 1.19 \pm .1$

*Not used in fit.

Table 6.4.2: Polarized Fluorescence from $^4S_{3/2}$.

Fluorescence from lowest $^4S_{3/2}$ level (E_1^L) to $^4I_{15/2}$ multiplet with magnetic field of 6T parallel to the z axis (see figure 5.2.1). Intensity parameters are the same as in table 6.4.1.

Final State	E parallel to z		E perpendicular to z	
	Theoretical Intensity	Experimental† Intensity	Theoretical Intensity	Experimental† Intensity
Z_1^L	-	laser line	0.17	laser line
Z_1^U	0.052	0.11 ± 0.005	-	-
Z_2^L	-	-	1.0	1 ± 0.2
Z_2^U	-	-	-	-
Z_3^L	0.31	0.09 ± 0.02	-	-
Z_3^U	-	-	0.19	0.21 ± 0.05
Z_4^L	-	-	-	-
Z_4^U	-	-	0.006	-
Z_5^L	4.49	>2.5	-	-
Z_5^U	-	-	0.08	-
Z_6^L	-	-	1.15	<0.4
Z_7^{L*}	-	-	0.66	0.47 ± 0.17
Z_6^U	-	-	-	-
Z_7^U	0.01	-	-	-
Z_8^L	-	-	-	-
Z_8^U	-	-	0.00002	-

*Note that Z_7^L is lower than Z_6^U. See Freeth (1980, figure 4.20).

†Freeth (1980)

obtained by selectively exciting only sites with the magnetic field parallel to the z axis (see Freeth 1980, Freeth and Jones 1981 for further details).

These calculations are not entirely satisfactory. The computed intensity of the transition to the Z_6 level (which was not measured accurately and so was not used in the fit) is too large and the calculated intensities for $\underline{E} \| z$ transitions are also too large. In addition the X_7^6 parameters are of the same order as the X_5^6 parameters whereas Porcher and Caro (1978) obtained X_5^6 parameters which were about three times the size of the X_7^6 ones.

In favour of the parameters a superposition model calculation of the odd crystal-field parameters indicated that $A^{5^-}(0)1^{-\tilde{0}^-}00$ and $A^{5^-}(1)1^{-\tilde{0}^-}00$ should be of the same sign, as should $A^{7^-}(0)1^{-\tilde{0}}00$ and $A^{7^-}(1)1^{-\tilde{0}^-}00$. This is consistent with the intensity parameters having the same sign (see eqn 6.1.2). Some of the anomalies may be caused by the neglect of crystal-field mixing between the $^4S_{3/2}$ multiplet and the ^4F and ^4H terms. However, the calculations show that the method works and provides further confirmation of Freeth's assignment of energy levels. More data is needed to allow the calculation of all intensity parameters. In particular, measurements for the hypersensitive transitions $^4I_{15/2} \leftrightarrow {}^2H_{11/2}$ and $^4I_{15/2} \leftrightarrow {}^4G_{11/2}$ are necessary to determine the $k = 2$ parameters.

CHAPTER 7

PAIR INTERACTIONS

In the last two chapters I have demonstrated the usefulness of point groups in analysing the states of single ions. In this chapter I shall apply the same methods to pairs of paramagnetic ions in crystals.

The construction of pair states for identical ions has been discussed by Judd (1959) and Vogel (1974) for specific cases. Because of the existence of electron antisymmetry one must be very clear about exactly what the action of the group operators is. The pair groups considered by Judd and Vogel include some operations which interchange the electrons between the ions but for the many electron case it is more convenient to consider a pair group which acts only on the wavefunctions.

Stedman and Newman (1971c) have shown that for Ir^{4+} pairs in the Hexachloroplatinates the factorizable part of the superexchange interaction is isotropic and Stedman (1979) has shown that electric and magnetic multipole interactions do not contribute to the spin Hamiltonian parameter E. I shall generalize these results.

(7.1) Transformation properties of pair states

A single paramagnetic ion in an otherwise perfect crystal has wave functions which transform as irreps of the

site symmetry group. If the ion is one of a pair then the symmetry is reduced but the original group and its subgroups are still approximate symmetries and irreps of these groups may be used to construct pair wavefunctions. I shall consider the case where the ions (and sites) are identical, in which case some of the operations of the pair group interchange the wave functions (and the electrons, depending on our definition). In all the examples considered by Judd (1959), Vogel (1974) and Stedman (1979) the pair group is the same as a subgroup of each site symmetry group (the only difference being the origin of the co-ordinates). This will be assumed for the remainder of this chapter. We label the sites a and b and define the following groups:

	G^p	pair group
H^a	H^b	local site symmetries
G^a	G^b	subgroups of H^a, H^b which are the same as G^p except for the co-ordinate origin.
	G^{ab}	performs the operations of G^a and G^b simultaneously.
	S_2^{ab}	interchanges wave-functions (not electrons) between sites.

The S_2 operation of S_2^{ab} is not an element of our G^p but G^p is contained in $S_2^{ab} \times G^{ab}$: every operation of G^p is a product of a G^{ab} operation and an S_2^{ab} operation. Now consider the irreps λ_1 and λ_2 of G^a and G^b. Since $G^a \times G^b \supset G^{ab}$ they are also irreps of G^{ab}. The combinations $|\lambda_1^a \lambda_2^b\rangle \pm |\lambda_2^a \lambda_1^b\rangle$ are representations of $G^{ab} \times S_2^{ab}$ and G^p.

Let $[\lambda_1\lambda_2]_{\pm}$ be the symmetric/antisymmetric part of the product $(\lambda_1+\lambda_2)$ x $(\lambda_1+\lambda_2)$. Then

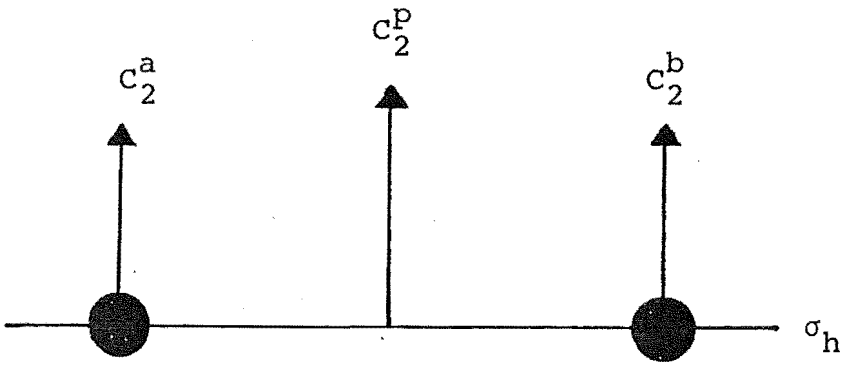
$$|\lambda_1\lambda_2\rangle + |\lambda_2\lambda_1\rangle \text{ transforms as } [\lambda_1\lambda_2]_+ \ (G^{ab}) \ 0(S_2^{ab})$$
$$\rightarrow [\lambda_1\lambda_2]_+ \ (G^p)$$
$$|\lambda_1\lambda_2\rangle - |\lambda_2\lambda_1\rangle \text{ transforms as } [\lambda_1\lambda_2]_- \ (G^{ab}) \ 1(S_2^{ab}) \qquad (7.1.1)$$
$$\rightarrow [\lambda_1\lambda_2]_- \ (G^p) \ x \ \tilde{\lambda}(G^p)$$

where $\tilde{\lambda}$ is the one dimensional irrep of G^p which has character -1 under operations which swap the ions and +1 under operations which do not. The first step follows from the definition of symmetric and antisymmetric products and the second from a simple character argument. The characters of $[\lambda_1\lambda_2]_+$ (G^{ab}) $0(S_2)$ under G^p are just the characters of $[\lambda_1\lambda_2]_+$ but for $[\lambda_1\lambda_2]_-$ (G^{ab}) $1(S_2)$ the characters change sign for the operations which interchange the ions. Multiplying by $\tilde{\lambda}$ has just this effect. Note that this process is intimately related to the imbedding of a rotation-reflection group in a rotation-inversion group (see appendix 4).

This analysis applies to ions with any number of electrons. The symmetry of the system under interchange of electrons may be treated separately. The analysis of antisymmeterization effects is similar to the case of mixed atomic configurations (see, for example Wybourne 1970), but the operators are no longer scalar under SO_3 because the symmetry is lower.

Judd (1959) and Vogel (1974) consider ions with only one electron, in which case the construction

Figure 7.1.1: Ir^{4+} pairs in the hexachloroplatinates



Ion a

G^a

Ion b

G^b

G^p

of determinantal product states is simple. If we redefine S_2^{ab} (and G^p) to interchange electrons as well as wavefunctions the electron antisymmetry reverses the S_2^{ab} symmetry in equation (7.1.1) and now

$$\begin{aligned}
&\{|\lambda_1\lambda_2\rangle + |\lambda_2\lambda_1\rangle\} \sim [\lambda_1\lambda_2]_+(G^{ab})\ 1(S_2) \\
&\qquad \to [\lambda_1\lambda_2]_+\ (G^p)\ \tilde{\lambda}(G^p) \\
&\{|\lambda_1\lambda_2\rangle - |\lambda_2\lambda_1\rangle\} \sim [\lambda_1\lambda_2]_-(G^{ab})\,0(S_2) \to [\lambda_1\lambda_2]_-(G^p)
\end{aligned} \tag{7.1.2}$$

(the curly brackets denote determinantal product states). For Judd's case (see fig 7.1.1) $G^p = C_{2h}$, $\tilde{\lambda} = 0^-$ (for notation see appendix 3) and

$$\begin{aligned}
\{|\tfrac{1}{2}\tfrac{1}{2}\rangle\} &\sim 1^+(C_{2h}^{ab})\ 1(S_2) \to 1^+ \times 0^- = 1^-(C_{2h}^p) \\
\{|-\tfrac{1}{2}-\tfrac{1}{2}\rangle\} &\sim 1^+(C_{2h}^{ab})\ 1(S_2) \to 1^+ \times 0^- = 1^-(C_{2h}^p) \\
\{|\tfrac{1}{2}-\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\tfrac{1}{2}\rangle\} &\sim 0^+(C_{2h}^{ab})\ 1(S_2) \to 0^+ \times 0^- = 0^-(C_{2h}^p) \\
\{|\tfrac{1}{2}-\tfrac{1}{2}\rangle - |-\tfrac{1}{2}\tfrac{1}{2}\rangle\} &\sim 0^+(C_{2h}^{ab})\ 0(S_2) \to \qquad\qquad 0^+(C_{2h}^p)
\end{aligned} \tag{7.1.3}$$

For Vogel's case $G^p = C_{3h}$ and $\tilde{\lambda} = 3$. The ground state quadruplet (his table 3) gives:

$$\begin{aligned}
\{|\tfrac{5}{2}\tfrac{5}{2}\rangle\} &\sim -1(C_{3h}^{ab})1(S_2^{ab}) \to -1 \times 3 = 2(C_{3h}^p) \\
\{|-\tfrac{5}{2}-\tfrac{5}{2}\rangle\} &\sim\ 1(C_{3h}^{ab})1(S_2^{ab}) \to\ 1 \times 3 = -2(C_{3h}^p) \\
\{|\tfrac{5}{2}-\tfrac{5}{2}\rangle + |-\tfrac{5}{2}\tfrac{5}{2}\rangle\} &\sim\ 0(C_{3h}^{ab})1(S_2^{ab}) \to\ 0 \times 3 =\ 3(C_{3h}^p) \\
\{|\tfrac{5}{2}-\tfrac{5}{2}\rangle - |-\tfrac{5}{2}\tfrac{5}{2}\rangle\} &\sim\ 0(C_{3h}^{ab})0(S_2^{ab}) \to\ \qquad\qquad 0(C_{3h}^p)
\end{aligned} \tag{7.1.4}$$

Vogel's table 3 does not agree with his rules. The irreps should be $\gamma_3, \gamma_2, \gamma_4$ and γ_{10} under his pair group (which is our $C_{3h}^{ab} \times S_2^{ab}$), which includes the operation of interchange of the electrons and wave-functions. Reduction to our pair group (C_{3h}^{p}) gives the results of equation (7.1.4) but note that $\gamma_{10} \rightarrow 0$ and not 3.

(7.2) One-electron Matrix Elements

We shall now use the concepts we have developed to obtain some simple, but general, results for ions with only one interacting electron or hole. Following Stedman (1979) we write a general matrix element as

$$\langle\{\phi_1^a(i)\ \phi_2^b(j)\}|\ O_{ij}\ |\{\phi_3^a(i)\ \phi_4^b(j)\}\rangle \qquad (7.2.1)$$

where O_{ij} is an effective two-electron, two particle Hamiltonian. Writing the determinantal states explicitly to give a direct and exchange term:

$$\langle\{\phi_1^a(i)\ \phi_2^b(j)\}|\ O_{ij}\ |\{\phi_3^a(i)\ \phi_4^b(j)\}\rangle = M_S - M_A \qquad (7.2.2)$$

$$= \langle\phi_1^a(i)\ \phi_2^b(j)|\ O_{ij}^S\ |\phi_3^a(i)\ \phi_4^b(j)\rangle$$

$$- \langle\phi_1^a(i)\ \phi_2^b(j)|\ O_{ij}^A\ |\phi_4^b(i)\ \phi_3^a(j)\rangle$$

We use the irreps of G^{ab} to label the states and operators. This may be extended to higher groups such as

O_3^{ab}, which performs O_3 operations similtaneously on each site. This sort of scheme was discussed by Copland and Newman (1972) but they used a JM basis rather than a point group basis. The usefulness of this scheme is that the $O_3^{ab} \supset G^{ab} \supset C_n^{ab}$ labels (where C_n is a cyclic subgroup of G, necessary to completely specify the basis) are just the single-ion $O_3 \supset G \supset C_n$ labels and the scheme may also be used for inequivalent ions. Since the operator O_{ij} is symmetric the requirement that the Hamiltonian be scalar under G^p implies that it is scalar under G^{ab}.

The operators may be written as a sum of products of one-centre or one-electron operators. For O_{ij}^S they are identical (one-centre and one-electron) but for O_{ij}^A we have either one-centre, two-electron operators

$$M_A = \sum_{\mu_a \mu_b} \Gamma^{\mu_a \mu_b} \langle \phi_1^a(i) | U^{\mu_a} | \phi_3^a(j) \rangle \langle \phi_2^b(j) | U^{\mu_b} | \phi_4^b(i) \rangle \qquad (7.2.3)$$

or one-electron, two-centre operators

$$M_A = \sum_{\mu_i \mu_j} J^{\mu_i \mu_j} \langle \phi_1^a(i) | \hat{U}^{\mu_i} | \phi_4^b(i) \rangle \langle \phi_2^b(j) | \hat{U}^{\mu_j} | \phi_3^a(j) \rangle \qquad (7.2.4)$$

where the μ labels are short for $O_3^{ab} \supset G^{ab} \supset C_n^{ab}$ labels $(ja\mu i)$. In what follows μ or ϕ will sometimes mean the irrep under G^{ab}, rather than a set of $O^{ab} \supset G^{ab} \supset C_n^{ab}$ irrep labels. The first scheme was used by Levy (1969) and the second by Copland and Newman (1972). Expressing the matrix elements in (7.2.3 and 4) as 3jm symbols and reduced matrix elements, via the Wigner-Eckart theorem, allows a direct derivation of

the relationship between the parameters (Γ and J) given by Copland and Newman (1972). Note that their summations are not over enough basis labels.

Triad conditions restrict the number of parameters. Since O_{ij} is scalar (i.e. transforms as the identity irrep O) under G^p and G^{ab} $\mu_a \times \mu_b \supset O(G^{ab})$ and $\mu_i \times \mu_j \supset O(G^{ab})$. O_{ij} is time reversal even, which restricts the sum of the O_3^{ab} quantum numbers of the operators ($j_i + j_j$ or $j_a + j_b$) to be even (see Cone and Wolf 1978). These restrictions still allow several dozen parameters for the C_{2h} and C_{3h} symmetries considered above. For electric and magnetic multipole interactions the parameters may be calculated (see Judd 1975) but for superexchange one must endeavour to make physically realistic simplifications, such as the factorizable model discussed in the next section.

(7.3) The factorizable model of Superexchange

The factorizable model (Bradbury and Newman 1968, Stedman and Newman 1971, Copland and Newman 1972) assumes that equation (7.2.4) may be factorized:

$$M_A = \sum_{\mu_i} J^{\mu_i} \langle \phi_1^a(i) | \hat{U}^{\mu_i} | \phi_4^b(i) \rangle \sum_{\mu_j} J^{\mu_j} \langle \phi_2^b(j) | \hat{U}^{\mu_j} | \phi_3^a(j) \rangle \qquad (7.3.1)$$

The requirement that the operators be scalar under G^p and G^{ab} now forces the $\hat{U}^{\mu_i}$ and $\hat{U}^{\mu_j}$ to be scalar under G^{ab}. Stedman and Newman (1971) showed that an interaction of this form gives an 'isotropic' contribution to the spin Hamiltonian (D = E = 0) for Ir^{4+} pairs in the Hexachloroplatinates.

We can generalize this to any pair of identical Kramers ions (with symmetry higher than C_1). The doubly degenerate ground state of one of the ions may be written as $\Lambda_\pm$ (e.g. $\pm\frac{1}{2}$ for the C_{2h} example in section 7.1). As discussed in section (7.1) the ground doublets of the pair form four irreps under G^p

$$\pi_1 = |\Lambda_+\Lambda_+\rangle$$

$$\pi_2 = |\Lambda_-\Lambda_-\rangle \qquad (7.3.2)$$

$$\pi_3 = (|\Lambda_+\Lambda_-\rangle + |\Lambda_-\Lambda_+\rangle \frac{1}{\sqrt{2}}$$

$$\pi_4 = (|\Lambda_+\Lambda_-\rangle - |\Lambda_-\Lambda_+\rangle)\frac{1}{\sqrt{2}}$$

and these will be the eigenfunctions of O_{ij}. Since, under $G^{ab}, \mu_i = \mu_j = 0$ (the identity) in equation (7.3.1) all off-diagonal matrix elements vanish and for the diagonal matrix elements:

$$H_{11} = H_{22} = H_{33} = -H_{44} \qquad (7.3.3)$$

so the pair states form a singlet and a triplet, which is equivalent to D = E = 0 in the spin-Hamiltonian formalism.

(7.4) Electric Multiplet Interaction

Now consider the electric multipole interactions (EMI) between the ions, which gives a contribution to M_S. The pair states λ_1 and λ_2 form a Kramers doublet which will only be split by an interaction term of the form:

$$H_{12} = \langle \Lambda_+ \Lambda_+ | O_{ij} | \Lambda_- \Lambda_- \rangle_s = \langle \Lambda_+ | \hat{U}_a | \Lambda_- \rangle \langle \Lambda_+ | \hat{U}_b | \Lambda_- \rangle \qquad (5.1)$$

This matrix element vanishes unless U_a and U_b are time reversal odd (see, for example, Stedman and Butler 1980) and therefore contains no contribution from the EMI mechanism, which consists of time reversal even operators. Thus the EMI contribution to the E parameter of the spin Hamiltonian formalism is zero since the doublet is not split. This was noted by Stedman (1979) for specific cases. Interactions which do split the doublet (superexchange, virtual phonon exchange) consist of time reversal odd components, though the whole operator is time reversal even.

(7.5) Conclusions

This discussion has clarified and generalized the problem of constructing pair states from single ion states. One must be very clear about what the action of the pair group is and I have argued that a pair group which acts only on wave functions is most useful because the extension to the many electron case is easier.

Some general results have been derived for electric multipole and factorizable superexchange interactions between Kramers ions. Previous proofs of these results were applicable only to special cases.

CHAPTER 8

CONCLUSIONS

Part of the work of this thesis has been of a mathematical nature. The applications considered used point group 3jms. These were calculated by the building up method and it was first necessary to understand the effect of the phase choices made in these calculations. That certain phase choices affect the orientation of the point group axes was demonstrated by computing tables of transformation coefficients. These transformation tables were essential in the solid state theory considered in this thesis. Some of the transformation coefficient tables appear in Butler (1981). Churcher and Stedman (1981 a and b) and Stedman and Minard (1981) have used the tables in their work on Raman selection rules and lattice strain.

The 6j symbols and 3jm factors for several unitary groups have been computed, and orientation type choices have been shown to exist in each of the unitary group imbeddings studied. My computer programs, used in this thesis to calculate point group matrix elements via the Wigner-Eckart theorem, have also been used for multiquark-hadron dissociation calculations (see Black and Wybourne 1981).

Several solid state applications have been considered in detail. Crystal field calculations in point group bases have been shown to possess the advantage, over the JM basis, of more natural basis states and parameters. By

surveying the available data and re-computing the crystal field splittings I have shown up many inconsistencies in the published analyses of Re^{3+} ions in tetragonal CaF_2 and SrF_2 sites. The ions for which the data is not contradictory show smooth trends in the crystal-field parameters. For these ions the superposition model has been used to estimate the local distortions of the sites. These estimates are consistent with endor experiments.

I have also discussed the calculation of the intensities of f^n-f^n transitions. The use of point group 3jms clarifies the Judd-Ofelt formalism. Fluorescence of Er^{3+} in CaF_2 has been used as an example and my calculations provide a reasonable explanation of the intensities.

The final application to be considered was the interaction between pairs of paramagnetic ions in crystals. Again the point group approach provides clarification to the formalism and several general results have been derived.

PUBLICATIONS

Appendix 1, 'Orientations of point groups-phase choices in the Racah-Wigner algebra', appears in J Phys A: Math. Gen. 13 (1980) 2889-2901 (with P.H. Butler).

Appendix 2, '3jm and 6j tables for some bases of SU_3 and SU_6' will be submitted to J Phys A: Math. Gen. (with R P Bickerstaff, P H Butler, M B Butts and R W Haase).

The results of chapter 5 have been prepared for publication and will be submitted to J Phys C: Solid State Phys. Under the title 'The point group crystal field and the superposition model for Re^{3+} ions in CaF_2 and SrF_2, (with P H Butler). Its submission has been delayed to allow C A Freeth to publish his experimental results.

APPENDIX 1

Orientations of point groups - phase choices in the Racah-Wigner algebra.

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Orientations of point groups—phase choices in the Racah–Wigner algebra

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Abstract. The SO_3-SO_2-3*jm*'s (the '3*j* symbols' of angular momentum) are known to incorporate no information about the orientation of axes and may be calculated from a knowledge of character theory alone, together with some freedom of choice of phases. For many point-group embeddings, at least once in every finite-group basis of SO_3, an extra phase choice arises in the 3*jm* calculation. We show that choosing this phase corresponds to choosing the orientation of the symmetry axes of the groups.

1. Introduction

Elementary applications of group theory in physics and chemistry yield qualitative information such as degeneracies and selection rules. To produce quantitative results requires the use of the Wigner–Eckart theorem and therefore the calculation of *jm* factors and *j* symbols (equivalently coupling and recoupling coefficients).

Most calculations proceed from an explicit definition of the symmetry axes or the generators of the group (e.g. Harnung and Schäffer 1972, Kibler and Grenet 1977, Kramer 1968). It has been shown that the *j* symbols and *jm* factors for arbitrary compact groups may be calculated from a knowledge of character theory alone and a methodology has been developed along these lines. It has been applied to SO_3, the embedding $SO_3 \supset SO_2$, the point groups T and C_3, the Lie groups in the chain $E_7 \supset SU_6 \times SU_3 \supset SU_2 \times SU_3 \times SU_3$ and the dihedral and cyclic groups. See Butler (1975, 1976, 1979), Donini (1979, pp 123–77), Butler and Wybourne (1976a, b), Butler *et al* (1978, 1979), Butler and Reid (1979) and Prasad and Bharathi (1980).

Several questions remain unanswered. Butler and Wybourne (1976a) were unable to demonstrate the completeness of their equations for all groups. Furthermore, in applications involving point groups it may be necessary to know where the symmetry axes lie. These calculations appear to contain no such information.

Within the Racah–Wigner algebra one may freely choose certain coupling and basis phases (Butler 1975, Butler and Wybourne 1976a). We shall show that for many point-group embeddings an extra phase choice (in addition to the above) must be made. This special phase choice affects the orientation of the symmetry axes of the group and we shall therefore refer to it as an orientation phase.

The embedding $D_3 \supset C_3$ is discussed in § 4 as an example. We show that the choice of orientation phase determines whether C_{2y} or C_{2x} (or neither) is in D_3. In § 5 orientation phases for other point groups are discussed. We show how the orientation of the symmetry axes may be determined once the 3*jm* factors have been calculated.

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All finite group bases of SO_3 involve at least one orientation phase. This corresponds to the freedom one has when choosing axes for point groups and is largely overlooked in calculations which fix the axes before calculating $3jm$'s. It has been noted by Boyle and Schäffer (1974) that different axis choices for the icosahedron are not equivalent. This is a special example of the phenomenon we discuss here.

We restrict ourselves to pure rotation groups in what follows. The properties of reflection–rotation and reflection–inversion groups are similar (but not trivially so—see Butler 1980).

2. Free phases in the Racah–Wigner algebra

The free phases which appear in the calculation of j symbols and jm factors were discussed by Butler (1975). Butler and Wybourne (1976a) gave a method of calculation which was based on building up from any chosen faithful irrep, called the primitive irrep. They proved that all $3jm$'s and $6j$'s could be calculated recursively once those containing the primitive irrep were known, but were unable to give a complete method for calculating primitive $6j$'s and $3jm$'s.

The reader is referred to the above for notation and definitions and for a discussion of the free phases involved in the calculation of j symbols. Here we shall be concerned only with jm factors which, unlike the j symbols, contain basis information, being dependent on the branching of the irreps of a group to its chosen subgroup. For example, the SO_3–SO_2-$3jm$ factors, the '$3j$ symbols' of angular momentum, depend on the SO_3-$6j$ symbols, and on the SO_3-SO_2-branching rules and nothing else (Butler 1976). In building up a set of primitive $3jm$ factors, certain branching multiplicity separations and choices of phase must be made. These choices are choices of the relationship among the partners of an irrep, and as such correspond to choices of the form of the irrep matrices (Butler 1975, equation (11.6)). We make these choices in the sequence used in Butler and Wybourne (1976a, § 6) and Butler and Reid (1979). The $2jm$ factors are first chosen, real and of a sign such that as many $3jm$ factors as possible are real. This action fixes the relationship between each pair of complex conjugate kets. Then for each (non-primitive) pair there is one free phase, which is fixed when the ket first arises in the $3jm$ calculation. In addition there may be orientation phases. We give examples in § 4 and § 5.

3. Transformation of basis

In the following sections we shall need to consider transformations between bases. Let the kets $|\lambda i\rangle$ form a $G \supset H \supset K$ basis and $|\lambda l\rangle'$ form a $G \supset H' \supset K$ basis. The transformation coefficients between the bases may be calculated by rewriting equation (11.6) of Butler (1975) as

$$\langle \lambda i | \lambda l \rangle' = \sum_{\substack{i_1 i_2 \\ l_1 l_2}} |\lambda| \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ i_1 & i_2 & i \end{pmatrix}^{*r} \langle \lambda_1 i_1 | \lambda_1 l_1 \rangle'^{*} \langle \lambda_2 i_1 | \lambda_2 l_2 \rangle'^{*} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ l_1 & l_2 & l \end{pmatrix}^{r}. \tag{3.1}$$

If, in this equation, λ_1 is chosen to be the primitive irrep we have a recursion relation for all transformation coefficients in terms of primitive G-H-K-$3jm$'s, primitive G-H'-K-$3jm$'s and the primitive transformation coefficients.

We label the identity and primitive irreps of point groups by 0 and $\frac{1}{2}$ respectively. The basis labels (i and l in (3.1)) may in practice be several point-group labels, depending on which group chain is used. For example, the partners of the irrep $\frac{1}{2}$ of SO_3 are $|\frac{1}{2}\frac{1}{2}\rangle$ and $|\frac{1}{2}-\frac{1}{2}\rangle$ in the JM basis. In the SO_3-D_∞-D_6-D_3-C_3 basis discussed in § 5 they are $|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\rangle$ and $|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\rangle$.

The primitive transformation coefficients are not all independent. Because of our $2jm$ choices ($\binom{0}{0}=\binom{\frac{1}{2}}{\frac{1}{2}}=1$ for all embeddings) one may deduce from equation (3.1) that

$$\langle 00|00\rangle' = 1$$
$$\langle \tfrac{1}{2}\tfrac{1}{2}|\tfrac{1}{2}\tfrac{1}{2}\rangle' = A = \langle \tfrac{1}{2}-\tfrac{1}{2}|\tfrac{1}{2}-\tfrac{1}{2}\rangle'^* \qquad \langle \tfrac{1}{2}-\tfrac{1}{2}|\tfrac{1}{2}\tfrac{1}{2}\rangle' = B = -\langle \tfrac{1}{2}\tfrac{1}{2}|\tfrac{1}{2}-\tfrac{1}{2}\rangle'^* \tag{3.2}$$

or equivalently

$$|\tfrac{1}{2}\tfrac{1}{2}\rangle' = |\tfrac{1}{2}\tfrac{1}{2}\rangle A + |\tfrac{1}{2}-\tfrac{1}{2}\rangle B \qquad |\tfrac{1}{2}-\tfrac{1}{2}\rangle' = |\tfrac{1}{2}\tfrac{1}{2}\rangle(-B^*) + |\tfrac{1}{2}-\tfrac{1}{2}\rangle A^*.$$

These restrictions are just those for having the primed kets related to the unprimed by a rotation $R(\alpha, \beta, \gamma)$ described by the Euler angles α, β, γ (see Messiah 1965, appendix C), where

$$A = e^{-i\alpha/2}\cos\tfrac{1}{2}\beta\, e^{-i\gamma/2} \qquad B = e^{i\alpha/2}\sin\tfrac{1}{2}\beta\, e^{-i\gamma/2}. \tag{3.3}$$

The point-group basis of SO_3 described by a given set of $3jm$ symbols may be transformed to the JM basis by using a particular A, B in equation (3.1). This is the converse of the approach of many other authors who first calculate the transformation coefficients in order to be able to calculate $3jm$ symbols. See for example Dobosh (1972), Golding and Newmarch (1977), Harnung and Schäffer (1972), Kibler and Grenet (1977) and Kramer (1968).

4. Example of $D_3 \supset C_3$

The j symbols and jm factors of all dihedral and cyclic groups were discussed by Butler and Reid (1979) and a possible choice of phases was suggested. In this section we shall analyse the repercussions of the orientation phase choices which occur in the embeddings $D_n \supset C_n$ and $D_{odd} \supset C_2$ by considering the embedding $D_3 \supset C_3$ in detail.

The above paper introduced a notation which used integers and half integers to label true and spin irreps respectively, in analogy to SO_3 and SO_2. The character table (table 1) gives the correspondence between our notation and those of some other authors.

The branching rules for $D_3 \supset C_3$ are

$$0\to 0 \qquad \tilde{0}\to 0 \qquad \tfrac{1}{2}\to \tfrac{1}{2}+-\tfrac{1}{2} \qquad \tfrac{3}{2}\to\tfrac{3}{2} \qquad -\tfrac{3}{2}\to\tfrac{3}{2}. \tag{4.1}$$

We noted in § 2 that all phase choices in the $3jm$ calculation are contained in the $2jm$'s and primitive $3jm$'s. The $2jm$'s are chosen in such a way that as many $3jm$'s as possible may be real. The set

$$\binom{0}{0}=1,\quad \binom{\frac{1}{2}}{\frac{1}{2}}=1,\quad \binom{\frac{1}{2}}{-\frac{1}{2}}=-1,\quad \binom{\tilde{0}}{0}=-1,$$
$$\binom{1}{1}=1,\quad \binom{1}{-1}=1,\quad \binom{\frac{3}{2}}{\frac{3}{2}}=1,\quad \binom{-\frac{3}{2}}{\frac{3}{2}}=-1 \tag{4.2}$$

Table 1. Character table for D_3. D_3 consists of: C_3: three-fold rotations about some axis; C_2': two-fold rotations about three axes perpendicular to the three-fold axis. Our irrep labels are shown, also those of Griffith (1961), Ballhausen (1962) and Koster *et al* (1963). We follow Lax (1974) in using the active convention for rotations.

Griffith, Ballhausen	Koster *et al*		E	$\bar{E}$	$2C_3$	$2\bar{C}_3$	$3C_2'$	$3\bar{C}_2'$
A_1	Γ_1	0	1	1	1	1	1	1
E'	Γ_4	$\frac{1}{2}$	2	−2	1	−1	0	0
A_2	Γ_2	$\tilde{0}$	1	1	1	1	−1	−1
E	Γ_3	1	2	2	−1	−1	0	0
E''	Γ_5	$\frac{3}{2}$	1	−1	−1	1	−i	i
	Γ_6	$-\frac{3}{2}$	1	−1	−1	1	i	−i

is suitable. There are only four inequivalent non-trivial primitive D_3-C_3-3*jm* factors:

$$\begin{pmatrix} \tilde{0} & \frac{1}{2} & \frac{1}{2} \\ 1 & -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \tag{4.3}$$

$$\begin{pmatrix} 1 & \frac{1}{2} & \frac{1}{2} \\ 1 & -\frac{1}{2} & -\frac{1}{2} \end{pmatrix} \tag{4.4}$$

$$\begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ \frac{3}{2} & 1 & \frac{1}{2} \end{pmatrix} \tag{4.5}$$

$$\begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ \frac{3}{2} & -1 & -\frac{1}{2} \end{pmatrix}. \tag{4.6}$$

The orthogonality relations (Butler and Wybourne 1976a, equations (35) and (36)) show that all have a norm of $1/\sqrt{2}$.

There is a free phase for each ket. However the phases of $|\frac{1}{2}-\frac{1}{2}\rangle$, $|1-1\rangle$ and $|\frac{3}{2}-\frac{3}{2}\rangle$ are related by the 2*jm* choices to their complex conjugates:

$$\begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} = \sqrt{2}\langle \tfrac{1}{2}\tfrac{1}{2}, \tfrac{1}{2}-\tfrac{1}{2}|00\rangle \qquad \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \sqrt{2}\langle 11, 1-1|00\rangle \qquad \begin{pmatrix} \frac{3}{2} \\ \frac{3}{2} \end{pmatrix} = \langle \tfrac{3}{2}\tfrac{3}{2}, -\tfrac{3}{2}\tfrac{3}{2}|00\rangle \tag{4.7}$$

(Butler and Wybourne 1976a, equation (29)). Furthermore, because the 3*jm*'s involve only relative phase information, the primitive ket $|\frac{1}{2}\frac{1}{2}\rangle$ does not contribute a freedom to the algebra. Therefore there are only three primitive 3*jm*'s which have this kind of phase freedom associated with them. Because $|\tilde{0}0\rangle$ is a real ket its choice is merely a sign. This corresponds to the fact that (4.3) is restricted to being real by the complex conjugation and column interchange symmetries (Butler and Wybourne 1976a, equations (37) and (38)). For (4.4) and (4.5) the choice is an arbitrary phase, corresponding to the kets $|11\rangle$ and $|\frac{3}{2}\frac{3}{2}\rangle$. We choose (4.3)–(4.5) as $1/\sqrt{2}$. At this stage there appear to be no free phases left and we would expect the calculation of all other 3*jm*'s to be straightforward. However, none of the equations (Butler and Wybourne 1976a, § 6–§ 8) tells us the phase of (4.6). This counters the speculation at the end of § 7 of Butler and Wybourne (1976a).

Let the phase of (4.6) relative to (4.3)–(4.5) be $e^{i\theta}$. We shall show that $e^{i\theta}$ is indeed free, but that it has an effect on the orientation of the group.

In order to do this we consider the transformation from the point-group basis $SO_3 \supset D_\infty \supset D_6 \supset D_3 \supset C_3$ to the JM basis, as discussed in § 2. We use the phase choices of Butler and Reid (1979) for the SO_3-D_∞-D_6-D_3 chain and we use the standard SO_3-SO_2-$3jm$'s. Taking $A = 1, B = 0$ in (3.2) and then using (3.1) recursively gives the $SO_3 \supset D_\infty \supset D_6 \supset D_3 \supset C_3$ kets (primed) in terms of the JM kets:

$$|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = |\tfrac{3}{2}\tfrac{3}{2}\rangle\, e^{i\theta}/\sqrt{2} + |\tfrac{3}{2}-\tfrac{3}{2}\rangle(-1\sqrt{2}) \qquad |\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}-\tfrac{3}{2}\tfrac{3}{2}\rangle' = |\tfrac{3}{2}\tfrac{3}{2}\rangle 1/\sqrt{2} + |\tfrac{3}{2}-\tfrac{3}{2}\rangle\, e^{-i\theta}/\sqrt{2}. \quad (4.8)$$

Rotation by an angle $\frac{2}{3}\pi$ about the z axis (Messiah 1965, equation (C63)) shows that the z axis is the three-fold axis:

$$R(\tfrac{2}{3}\pi, z)|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = -|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' \quad (4.9)$$

(see figure 1). The two-fold axes are therefore in the xy plane.

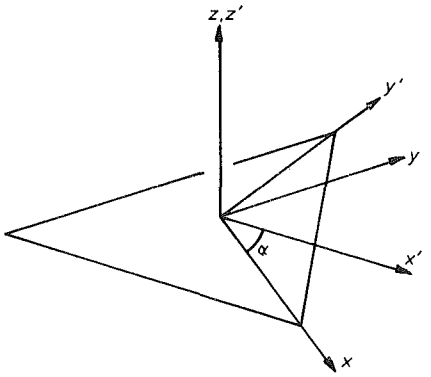

Figure 1. Axes for D_3. The unprimed and primed axes refer to equations (4.10) and (4.11) respectively. $\alpha = \pi/6$ corresponds to $\theta = \pi/2$ in (4.14).

If $\theta = 0$ in (4.8), then

$$R(\pi, x)|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = -i|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' \qquad R(\pi, y)|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = -|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}-\tfrac{3}{2}\tfrac{3}{2}\rangle' \quad (4.10)$$

(Messiah 1965, equations (C61) and (C62)). In this case the operator $R(\pi, x)$ is contained in the group while $R(\pi, y)$ is not. If $\theta = \frac{1}{2}\pi$ then

$$R(\pi, x)|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = -|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}-\tfrac{3}{2}\tfrac{3}{2}\rangle' \qquad R(\pi, y)|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = -i|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle'. \quad (4.11)$$

$R(\pi, y)$ is now in the group (see figure 1). (For other choices of the phase $e^{i\theta}$ neither $R(\pi, x)$ nor $R(\pi, y)$ is in the group.)

Of the phase choices of (4.3)–(4.6), only the phase of (4.6) relative to (4.5) affects the orientation of the two-fold axes. This may be seen by repeating the above arguments with arbitrary phases for (4.3)–(4.6).

Now consider two sets of $3jm$'s for $D_3 \supset C_3$ for which the phase of (4.6) has been chosen differently (but (4.3)–(4.5) are identical):

$$\begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ \frac{3}{2} & -1 & -\frac{1}{2} \end{pmatrix}' = e^{i\theta}\begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ \frac{3}{2} & -1 & -\frac{1}{2} \end{pmatrix}. \quad (4.12)$$

We may transform between two SO_3-D_∞-D_6-D_3-C_3 bases, one with the unprimed and the other the primed choice, and also rotate the primed basis by an angle α about the z

axis by choosing $A = e^{-i\alpha/2}$, $B = 0$ in (3.3). The relationship between the $J = \frac{3}{2}$ kets is then:

$$\langle \tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = \tfrac{1}{2}(e^{i\theta}\, e^{-3i\alpha/2} + e^{3i\alpha/2})$$
$$\langle \tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2} - \tfrac{3}{2}\tfrac{3}{2}|\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2}\rangle' = \tfrac{1}{2}(e^{i\theta}\, e^{-3i\alpha/2} - e^{3i\alpha/2}). \tag{4.13}$$

If the unprimed and the primed D_3 irreps are not to be mixed, then one requires

$$e^{i\theta} = e^{3i\alpha}. \tag{4.14}$$

Thus if $\alpha = 0$, $e^{i\theta} = 1$ only, while if $\theta = 0$ then α must be a multiple of $\frac{2}{3}\pi$. Observe that a $\frac{2}{3}\pi$ rotation about the z axis is a symmetry operation of D_3. See figure 1.

We have shown that a special orientation phase choice exists which changes the orientation of the group D_3 in the C_3 basis. (4.14) proves that it is equivalent to a rotation about the z axis. In the next section we shall discuss similar phase choices for other groups.

5. Orientation phases in the other point groups

In § 4 we showed that for $D_3 \supset C_3$ there was a phase choice which was equivalent to a rotation about the z axis. For all $D_n \supset C_n$, $D_{odd} \supset C_2$ and $T \supset C_3$ a similar orientation phase choice exists. For many embeddings, e.g. $SO_3 \supset SO_2$, $SO_3 \supset O$, $D_{mn} \supset D_n$, $O \supset D_4$ and $O \supset T$, no such choice exists. For $O \supset D_3$, $T \supset D_2$, $K \supset T$ and $K \supset D_5$ we must choose between a pair of double roots. In the double root cases the choice is still equivalent to a rotation about the z axis but now there are only two possible orientations.

As an example of the double root case we consider $T \supset D_2$. Butler (1979) proved that some $3jm$ factors of $T \supset D_2$ must be complex. In the calculation of $T \supset D_2$ $3jm$'s by the methods described in § 4, a similar problem arises—once all the phases are fixed. The real part and the magnitude of

$$\begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ \frac{1}{2} & 1 & \frac{1}{2} \end{pmatrix}^{T}_{D_2} = \frac{-1}{2\sqrt{3}} \pm \frac{i}{2} \tag{5.1}$$

may be calculated, but not the sign of the imaginary part (table 2 gives the correspondence between our notation and some others). As in § 4 the choice affects the orientation of the tetrahedron and corresponds to the two distinct ways of orienting a tetrahedron about D_2 axes (see figure 2).

The two phase choices, like the figures, are related by a $\frac{1}{2}\pi$ rotation. Table 3 shows a transformation between the $O \supset T \supset D_2 \supset C_2$ bases with two root choices in which a rotation of $\frac{1}{2}\pi$ about the z axis has been used to bring the two tetrahedra into coincidence. (The fact that $D_2 \supset C_2$ contains an orientation phase is irrelevant because it is the same in both schemes.) Note that the rotation mixes the irreps of D_2 but not O. This is because a $\frac{1}{2}\pi$ rotation about the z axis is an octahedral operation (with this orientation), but not a tetrahedral or D_2 operation. In tables 3, 4 and 5 kets in one basis are written as a sum of kets in another basis in the format: |ket in one basis⟩ = Σ_{basis} |ket in the other basis⟩ × (transformation coefficient). In table 3 the labels on both sides of the equations are irrep labels for the groups O, T, D_2 and C_2 (see table 2).

Table 2. Correspondence between our notation and that of Koster *et al* (1963) and Griffith (1961).

Cyclic Group C_2								
	0	$\frac{1}{2}$	$-\frac{1}{2}$	1				
Koster *et al*	Γ_1	Γ_3	Γ_4	Γ_2				
Dihedral Group D_2								
	0	$\frac{1}{2}$	$\tilde{0}$	1	$\tilde{1}$			
Koster *et al*	Γ_1	Γ_5	Γ_3	Γ_2	Γ_4			
Griffith	A_1	E′	B_1	B_2	B_3			
Cyclic Group C_4								
	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2
Koster *et al*	Γ_1	Γ_5	Γ_6	Γ_3	Γ_4	Γ_8	Γ_7	Γ_2
Dihedral Group D_4								
	0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{3}{2}$	2	$\tilde{2}$	
Koster *et al*	Γ_1	Γ_6	Γ_2	Γ_5	Γ_7	Γ_3	Γ_4	
Griffith	A_1	E′	A_2	E	E″	B_1	B_2	
Tetrahedral Group T								
	0	$\frac{1}{2}$	1	$\frac{3}{2}$	$-\frac{3}{2}$	2	-2	
Koster *et al*	Γ_1	Γ_5	Γ_4	Γ_6	Γ_7	Γ_2	Γ_3	
Griffith	A_1	E′	T	E″	E‴	E		
Octahedral Group O								
	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\tilde{1}$	$\tilde{\frac{1}{2}}$	$\tilde{0}$
Koster *et al*	Γ_1	Γ_6	Γ_4	Γ_8	Γ_3	Γ_5	Γ_7	Γ_2
Griffith	A_1	E′	T_1	U′	E	T_2	E″	A_2

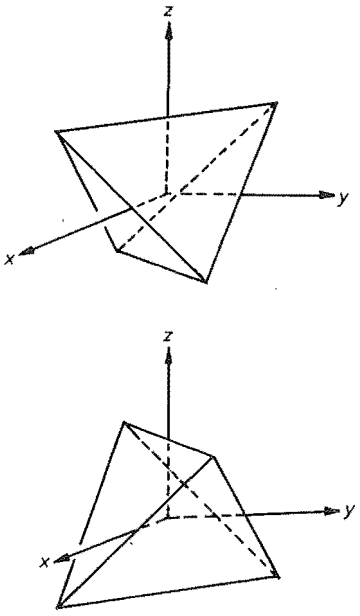

Figure 2. Orientations of a tetrahedron about D_2 axes.

Table 3. Transformation between two $O \supset T \supset D_2 \supset C_2$ bases. The format is: |ket with +ve root choice in equation (5.1)⟩ = |ket with −ve choice⟩ × (transformation coefficient). The labels are O, T, D_2 and C_2 irrep labels (see table 2).

| 0 0 0 0⟩	=	| 0 0 0 0⟩ + 1
| ½ ½ ½ ½⟩	=	| ½ ½ ½ ½⟩ + 1/√2 − i/√2
| ½ ½ ½ -½⟩	=	| ½ ½ ½ -½⟩ + 1/√2 + i/√2
| 1 1 1̃ 0⟩	=	| 1 1 1̃ 0⟩ + 1
| 1 1 1 1⟩	=	| 1 1 1̃ 1⟩ + i
| 1 1 1̃ 1⟩	=	| 1 1 1 1⟩ + i
| ⅔ ⅔ ½ ½⟩	=	| ⅔ ⅔ ½ ½⟩ + 1/√2 − i/√2
| ⅔ ⅔ ½ -½⟩	=	| ⅔ ⅔ ½ -½⟩ + 1/√2 + i/√2
| ⅔ -⅔ ½ ½⟩	=	| ⅔ -⅔ ½ ½⟩ + 1/√2 − i/√2
| ⅔ -⅔ ½ -½⟩	=	| ⅔ -⅔ ½ -½⟩ + 1/√2 + i/√2
| 2 2 0 0⟩	=	| 2 2 0 0⟩ + 1
| 2 -2 0 0⟩	=	| 2 -2 0 0⟩ + 1
| 1̃ 1 1̃ 0⟩	=	| 1̃ 1 1̃ 0⟩ + 1
| 1̃ 1 1 1⟩	=	| 1̃ 1 1̃ 1⟩ + i
| 1̃ 1 1̃ 1⟩	=	| 1̃ 1 1 1⟩ + i
| ½̃ ½ ½ ½⟩	=	| ½̃ ½ ½ ½⟩ + 1/√2 − i/√2
| ½̃ ½ ½ -½⟩	=	| ½̃ ½ ½ -½⟩ + 1/√2 + i/√2
| 0̃ 0 0 0⟩	=	| 0̃ 0 0 0⟩ + 1

Table 4. Transformation of $SO_3 \supset O \supset D_4 \supset C_4$ to the JM basis with the $D_4 \supset C_4$ orientation phase choice of equation (5.2). The format is: $|SO_3OD_4C_4\ \text{ket}\rangle = \Sigma_M\ |\text{JM ket}\rangle \times$ (transformation coefficient).

| 0 0 0 0⟩	=	| 0 0⟩ + 1
| ½ ½ ½ ½⟩	=	| ½ ½⟩ + 1
| ½ ½ ½ -½⟩	=	| ½ -½⟩ + 1
| 1 1 1̃ 0⟩	=	| 1 0⟩ + 1
| 1 1 1 1⟩	=	| 1 1⟩ − 1
| 1 1 1 -1⟩	=	| 1 -1⟩ − 1
| ⅔ ⅔ ½ ½⟩	=	| ⅔ ½⟩ + 1
| ⅔ ⅔ ½ -½⟩	=	| ⅔ -½⟩ − 1
| ⅔ ⅔ ⅔ ⅔⟩	=	| ⅔ ⅔⟩ + 1
| ⅔ ⅔ ⅔ -⅔⟩	=	| ⅔ -⅔⟩ + 1

Table 4.—continued.

$$
\begin{aligned}
|\,2\ 2\ 0\ 0\rangle &= |\,2\ 0\rangle - 1\\
|\,2\ 2\ 2\ 2\rangle &= |\,2\ 2\rangle - 1/\sqrt{2} + |\,2\text{-}2\rangle - 1/\sqrt{2}\\
|\,2\ \tilde{1}\ 1\ 1\rangle &= |\,2\ 1\rangle - 1\\
|\,2\ \tilde{1}\ 1\text{-}1\rangle &= |\,2\text{-}1\rangle + 1\\
|\,2\ \tilde{1}\ \tilde{2}\ 2\rangle &= |\,2\ 2\rangle + 1/\sqrt{2} + |\,2\text{-}2\rangle - 1/\sqrt{2}
\end{aligned}
$$

$$
\begin{aligned}
|\,\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle &= |\,\tfrac{5}{2}\ \tfrac{1}{2}\rangle + 1\\
|\,\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle &= |\,\tfrac{5}{2}\text{-}\tfrac{1}{2}\rangle + 1\\
|\,\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle &= |\,\tfrac{5}{2}\ \tfrac{3}{2}\rangle - 1/\sqrt{2.3} + |\,\tfrac{5}{2}\text{-}\tfrac{5}{2}\rangle - \sqrt{5}/\sqrt{2.3}\\
|\,\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle &= |\,\tfrac{5}{2}\ \tfrac{5}{2}\rangle + \sqrt{5}/\sqrt{2.3} + |\,\tfrac{5}{2}\text{-}\tfrac{3}{2}\rangle + 1/\sqrt{2.3}\\
|\,\tfrac{5}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle &= |\,\tfrac{5}{2}\ \tfrac{3}{2}\rangle + \sqrt{5}/\sqrt{2.3} + |\,\tfrac{5}{2}\text{-}\tfrac{5}{2}\rangle - 1/\sqrt{2.3}\\
|\,\tfrac{5}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle &= |\,\tfrac{5}{2}\ \tfrac{5}{2}\rangle + 1/\sqrt{2.3} + |\,\tfrac{5}{2}\text{-}\tfrac{3}{2}\rangle - \sqrt{5}/\sqrt{2.3}
\end{aligned}
$$

$$
\begin{aligned}
|\,3\ 1\ \tilde{0}\ 0\rangle &= |\,3\ 0\rangle - 1\\
|\,3\ 1\ 1\ 1\rangle &= |\,3\ 1\rangle - \sqrt{3}/2\sqrt{2} + |\,3\text{-}3\rangle - \sqrt{5}/2\sqrt{2}\\
|\,3\ 1\ 1\text{-}1\rangle &= |\,3\ 3\rangle - \sqrt{5}/2\sqrt{2} + |\,3\text{-}1\rangle - \sqrt{3}/2\sqrt{2}\\
|\,3\ \tilde{1}\ 1\ 1\rangle &= |\,3\ 1\rangle - \sqrt{5}/2\sqrt{2} + |\,3\text{-}3\rangle + \sqrt{3}/2\sqrt{2}\\
|\,3\ \tilde{1}\ 1\text{-}1\rangle &= |\,3\ 3\rangle + \sqrt{3}/2\sqrt{2} + |\,3\text{-}1\rangle - \sqrt{5}/2\sqrt{2}\\
|\,3\ \tilde{1}\ \tilde{2}\ 2\rangle &= |\,3\ 2\rangle - 1/\sqrt{2} + |\,3\text{-}2\rangle - 1/\sqrt{2}\\
|\,3\ \tilde{0}\ 2\ 2\rangle &= |\,3\ 2\rangle - 1/\sqrt{2} + |\,3\text{-}2\rangle + 1/\sqrt{2}
\end{aligned}
$$

$$
\begin{aligned}
|\,\tfrac{7}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{1}{2}\rangle - \sqrt{7}/2\sqrt{3} + |\,\tfrac{7}{2}\text{-}\tfrac{7}{2}\rangle - \sqrt{5}/2\sqrt{3}\\
|\,\tfrac{7}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{7}{2}\rangle + \sqrt{5}/2\sqrt{3} + |\,\tfrac{7}{2}\text{-}\tfrac{1}{2}\rangle + \sqrt{7}/2\sqrt{3}\\
|\,\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{1}{2}\rangle - \sqrt{5}/2\sqrt{3} + |\,\tfrac{7}{2}\text{-}\tfrac{7}{2}\rangle + \sqrt{7}/2\sqrt{3}\\
|\,\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{7}{2}\rangle - \sqrt{7}/2\sqrt{3} + |\,\tfrac{7}{2}\text{-}\tfrac{1}{2}\rangle + \sqrt{5}/2\sqrt{3}\\
|\,\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{3}{2}\rangle + \sqrt{3}/2 + |\,\tfrac{7}{2}\text{-}\tfrac{5}{2}\rangle + 1/2\\
|\,\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{5}{2}\rangle + 1/2 + |\,\tfrac{7}{2}\text{-}\tfrac{3}{2}\rangle + \sqrt{3}/2\\
|\,\tfrac{7}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{3}{2}\rangle + 1/2 + |\,\tfrac{7}{2}\text{-}\tfrac{5}{2}\rangle - \sqrt{3}/2\\
|\,\tfrac{7}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle &= |\,\tfrac{7}{2}\ \tfrac{5}{2}\rangle - \sqrt{3}/2 + |\,\tfrac{7}{2}\text{-}\tfrac{3}{2}\rangle + 1/2
\end{aligned}
$$

$$
\begin{aligned}
|\,4\ 0\ 0\ 0\rangle &= |\,4\ 4\rangle + \sqrt{5}/2\sqrt{2.3} + |\,4\ 0\rangle + \sqrt{7}/2\sqrt{3} + |\,4\text{-}4\rangle + \sqrt{5}/2\sqrt{2.3}\\
|\,4\ 1\ \tilde{0}\ 0\rangle &= |\,4\ 4\rangle + 1/\sqrt{2} + |\,4\text{-}4\rangle - 1/\sqrt{2}\\
|\,4\ 1\ 1\ 1\rangle &= |\,4\ 1\rangle + \sqrt{7}/2\sqrt{2} + |\,4\text{-}3\rangle + 1/2\sqrt{2}\\
|\,4\ 1\ 1\text{-}1\rangle &= |\,4\ 3\rangle - 1/2\sqrt{2} + |\,4\text{-}1\rangle - \sqrt{7}/2\sqrt{2}\\
|\,4\ 2\ 0\ 0\rangle &= |\,4\ 4\rangle - \sqrt{7}/2\sqrt{2.3} + |\,4\ 0\rangle + \sqrt{5}/2\sqrt{3} + |\,4\text{-}4\rangle - \sqrt{7}/2\sqrt{2.3}\\
|\,4\ 2\ 2\ 2\rangle &= |\,4\ 2\rangle - 1/\sqrt{2} + |\,4\text{-}2\rangle - 1/\sqrt{2}\\
|\,4\ \tilde{1}\ 1\ 1\rangle &= |\,4\ 1\rangle + 1/2\sqrt{2} + |\,4\text{-}3\rangle - \sqrt{7}/2\sqrt{2}\\
|\,4\ \tilde{1}\ 1\text{-}1\rangle &= |\,4\ 3\rangle + \sqrt{7}/2\sqrt{2} + |\,4\text{-}1\rangle - 1/2\sqrt{2}\\
|\,4\ \tilde{1}\ \tilde{2}\ 2\rangle &= |\,4\ 2\rangle + 1/\sqrt{2} + |\,4\text{-}2\rangle - 1/\sqrt{2}
\end{aligned}
$$

Table 5. Transformation of $SO_3 \supset O \supset D_4 \supset C_4$ to the JM basis with the orientation phase choice of equation (5.3). The format is: $|SO_3OD_4C_4\ \text{ket}\rangle = \Sigma_M\ |\text{JM ket}\rangle \times (\text{transformation coefficient})$.

$$
\begin{aligned}
|\,0\ 0\ 0\ 0\rangle &= |\,0\ 0\rangle + 1\\
|\,\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle &= |\,\tfrac{1}{2}\ \tfrac{1}{2}\rangle + 1\\
|\,\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle &= |\,\tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle + 1
\end{aligned}
$$

Table 5.—continued

$$|1\ 1\ \tilde{0}\ 0\rangle = |1\ 0\rangle + 1$$
$$|1\ 1\ 1\ 1\rangle = |1\ 1\rangle - 1$$
$$|1\ 1\ 1\text{-}1\rangle = |1\text{-}1\rangle - 1$$

$$|\tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = |\tfrac{3}{2}\ \tfrac{1}{2}\rangle + 1$$
$$|\tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle = |\tfrac{3}{2}\text{-}\tfrac{1}{2}\rangle - 1$$
$$|\tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = |\tfrac{3}{2}\ \tfrac{3}{2}\rangle + 1$$
$$|\tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle = |\tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle + 1$$

$$|2\ 2\ 0\ 0\rangle = |2\ 0\rangle - 1$$
$$|2\ 2\ 2\ 2\rangle = |2\ 2\rangle + i/\sqrt{2} + |2\text{-}2\rangle - i/\sqrt{2}$$
$$|2\ \tilde{1}\ 1\ 1\rangle = |2\ 1\rangle - 1$$
$$|2\ \tilde{1}\ 1\text{-}1\rangle = |2\text{-}1\rangle + 1$$
$$|2\ \tilde{1}\ \tilde{2}\ 2\rangle = |2\ 2\rangle - i/\sqrt{2} + |2\text{-}2\rangle - i/\sqrt{2}$$

$$|\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = |\tfrac{5}{2}\ \tfrac{1}{2}\rangle + 1$$
$$|\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle = |\tfrac{5}{2}\text{-}\tfrac{1}{2}\rangle + 1$$
$$|\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = |\tfrac{5}{2}\ \tfrac{3}{2}\rangle - 1/\sqrt{2.3} + |\tfrac{5}{2}\text{-}\tfrac{5}{2}\rangle + \sqrt{5}/\sqrt{2.3}$$
$$|\tfrac{5}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle = |\tfrac{5}{2}\ \tfrac{5}{2}\rangle - \sqrt{5}/\sqrt{2.3} + |\tfrac{5}{2}\text{-}\tfrac{3}{2}\rangle + 1/\sqrt{2.3}$$
$$|\tfrac{5}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = |\tfrac{5}{2}\ \tfrac{3}{2}\rangle + \sqrt{5}/\sqrt{2.3} + |\tfrac{5}{2}\text{-}\tfrac{5}{2}\rangle + 1/\sqrt{2.3}$$
$$|\tfrac{5}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle = |\tfrac{5}{2}\ \tfrac{5}{2}\rangle - 1/\sqrt{2.3} + |\tfrac{5}{2}\text{-}\tfrac{3}{2}\rangle - \sqrt{5}/\sqrt{2.3}$$

$$|3\ 1\ \tilde{0}\ 0\rangle = |3\ 0\rangle - 1$$
$$|3\ 1\ 1\ 1\rangle = |3\ 1\rangle - \sqrt{3}/2\sqrt{2} + |3\text{-}3\rangle + \sqrt{5}/2\sqrt{2}$$
$$|3\ 1\ 1\text{-}1\rangle = |3\ 3\rangle + \sqrt{5}/2\sqrt{2} + |3\text{-}1\rangle - \sqrt{3}/2\sqrt{2}$$
$$|3\ \tilde{1}\ 1\ 1\rangle = |3\ 1\rangle - \sqrt{5}/2\sqrt{2} + |3\text{-}3\rangle - \sqrt{3}/2\sqrt{2}$$
$$|3\ \tilde{1}\ 1\text{-}1\rangle = |3\ 3\rangle - \sqrt{3}/2\sqrt{2} + |3\text{-}1\rangle - \sqrt{5}/2\sqrt{2}$$
$$|3\ \tilde{1}\ \tilde{2}\ 2\rangle = |3\ 2\rangle + i/\sqrt{2} + |3\text{-}2\rangle - i/\sqrt{2}$$
$$|3\ \tilde{0}\ 2\ 2\rangle = |3\ 2\rangle + i/\sqrt{2} + |3\text{-}2\rangle + i/\sqrt{2}$$

$$|\tfrac{7}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = |\tfrac{7}{2}\ \tfrac{1}{2}\rangle - \sqrt{7}/2\sqrt{3} + |\tfrac{7}{2}\text{-}\tfrac{7}{2}\rangle + \sqrt{5}/2\sqrt{3}$$
$$|\tfrac{7}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle = |\tfrac{7}{2}\ \tfrac{7}{2}\rangle - \sqrt{5}/2\sqrt{3} + |\tfrac{7}{2}\text{-}\tfrac{1}{2}\rangle + \sqrt{7}/2\sqrt{3}$$
$$|\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = |\tfrac{7}{2}\ \tfrac{1}{2}\rangle - \sqrt{5}/2\sqrt{3} + |\tfrac{7}{2}\text{-}\tfrac{7}{2}\rangle - \sqrt{7}/2\sqrt{3}$$
$$|\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle = |\tfrac{7}{2}\ \tfrac{7}{2}\rangle + \sqrt{7}/2\sqrt{3} + |\tfrac{7}{2}\text{-}\tfrac{1}{2}\rangle + \sqrt{5}/2\sqrt{3}$$
$$|\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = |\tfrac{7}{2}\ \tfrac{3}{2}\rangle + \sqrt{3}/2 + |\tfrac{7}{2}\text{-}\tfrac{5}{2}\rangle - 1/2$$
$$|\tfrac{7}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle = |\tfrac{7}{2}\ \tfrac{5}{2}\rangle - 1/2 + |\tfrac{7}{2}\text{-}\tfrac{3}{2}\rangle + \sqrt{3}/2$$
$$|\tfrac{7}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = |\tfrac{7}{2}\ \tfrac{3}{2}\rangle + 1/2 + |\tfrac{7}{2}\text{-}\tfrac{5}{2}\rangle + \sqrt{3}/2$$
$$|\tfrac{7}{2}\ \tilde{\tfrac{1}{2}}\ \tfrac{3}{2}\text{-}\tfrac{3}{2}\rangle = |\tfrac{7}{2}\ \tfrac{5}{2}\rangle + \sqrt{3}/2 + |\tfrac{7}{2}\text{-}\tfrac{3}{2}\rangle + 1/2$$

$$|4\ 0\ 0\ 0\rangle = |4\ 4\rangle - \sqrt{5}/2\sqrt{2.3} + |4\ 0\rangle + \sqrt{7}/2\sqrt{3} + |4\text{-}4\rangle - \sqrt{5}/2\sqrt{2.3}$$
$$|4\ 1\ \tilde{0}\ 0\rangle = |4\ 4\rangle - 1/\sqrt{2} + |4\text{-}4\rangle + 1/\sqrt{2}$$
$$|4\ 1\ 1\ 1\rangle = |4\ 1\rangle + \sqrt{7}/2\sqrt{2} + |4\text{-}3\rangle - 1/2\sqrt{2}$$
$$|4\ 1\ 1\text{-}1\rangle = |4\ 3\rangle + 1/2\sqrt{2} + |4\text{-}1\rangle - \sqrt{7}/2\sqrt{2}$$
$$|4\ 2\ 0\ 0\rangle = |4\ 4\rangle + \sqrt{7}/2\sqrt{2.3} + |4\ 0\rangle + \sqrt{5}/2\sqrt{3} + |4\text{-}4\rangle + \sqrt{7}/2\sqrt{2.3}$$
$$|4\ 2\ 2\ 2\rangle = |4\ 2\rangle + i/\sqrt{2} + |4\text{-}2\rangle - i/\sqrt{2}$$
$$|4\ \tilde{1}\ 1\ 1\rangle = |4\ 1\rangle + 1/2\sqrt{2} + |4\text{-}3\rangle + \sqrt{7}/2\sqrt{2}$$
$$|4\ \tilde{1}\ 1\text{-}1\rangle = |4\ 3\rangle - \sqrt{7}/2\sqrt{2} + |4\text{-}1\rangle - 1/2\sqrt{2}$$
$$|4\ \tilde{1}\ \tilde{2}\ 2\rangle = |4\ 2\rangle - i/\sqrt{2} + |4\text{-}2\rangle - i/\sqrt{2}$$

Boyle and Schäffer (1974) showed that orientations of the icosahedron unrelated by icosahedral operations ($\pi/2$ apart) gave distinct icosahedral tensors. Their two orientations correspond to the scheme $K \supset T \supset D_2 \supset C_2$ with the two choices of root for $T \supset D_2$.

Since all finite group bases of SO_3 contain an embedding of a cyclic group in a dihedral group or the embedding $T \supset C_3$ (Koster *et al* 1963), any application of such bases involves an orientation phase. This corresponds to the freedom one has to choose the orientation of the x and y axes, the z axis being determined, up to group operations, by the choice of groups. For $SO_3 \supset O \supset D_3 \supset C_3$ the z axis is three-fold, through a corner of the cube; for $SO_3 \supset O \supset D_4 \supset C_4$ the z axis is four-fold, through a face of the cube.

Consider $SO_3 \supset O \supset D_4 \supset C_4$. Tables 4 and 5 show the transformation of this basis to the JM basis for two particular choices of orientation phase for $D_4 \supset C_4$:

$$\begin{pmatrix} 2 & \frac{3}{2} & \frac{1}{2} \\ 2 & \frac{3}{2} & \frac{1}{2} \end{pmatrix}^{D_4}_{C_4} = \frac{+1}{\sqrt{2}} \tag{5.2}$$

$$\begin{pmatrix} 2 & \frac{3}{2} & \frac{1}{2} \\ 2 & \frac{3}{2} & \frac{1}{2} \end{pmatrix}^{D_4}_{C_4} = \frac{i}{\sqrt{2}}. \tag{5.3}$$

A calculation of the character of the irrep $\tilde{0}$ of O under a two-fold rotation about the y axis (see § 4) shows that the choice (5.2) corresponds to having the x and y axes through the faces of the cube and (5.3) to having the x and y axes through the edges. See figure 3 and the character tables of Koster *et al* (1963). In the former case the rotation matrices (Messiah 1965, appendix C) may be used to show that the 111 axis is a three-fold axis of O. In the latter the 101 and 110 axes are three-fold.

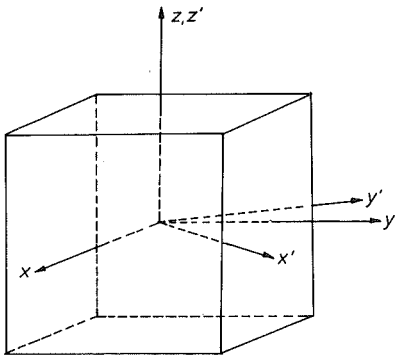

Figure 3. Axes of a cube. The unprimed and primed axes correspond to the choices (5.2) and (5.3) respectively.

The fourth-order scalar operator for octahedral symmetry with a four-fold z axis is commonly written

$$C^4 = C^4_0 + \sqrt{5/14}(C^4_4 + C^4_{-4}) \tag{5.4}$$

(e.g. Hutchings 1964). This corresponds to table 4—in table 5 the first sign in (5.4) is changed. Table 4 is similar to the table of Ballhausen (1962, p 95), the differences being due to the free (non-orientation) phases for the $SO_3 \supset O \supset D_4 \supset C_4$ kets.

6. Branching rules

The orientation phase problem must not be confused with another problem—the existence of several sets of valid branching rules for some point-group embeddings. Branching rules depend on the labelling of classes, for this determines which operations are to be discarded on going from the group to the subgroup.

An extreme case is the embedding $D_2 \supset C_2$. There are, in addition to the identity, three one-dimensional irreps of D_2: $\tilde{0}$, 1 and $\tilde{1}$. These irreps are not distinguished by the product rules of D_2, and three different $D_2 \supset C_2$ branching rules are possible since any one of these one-dimensional irreps of D_2 may reduce to the identity irrep of C_2. The usual branching (Koster *et al* 1963) is $\tilde{0} \rightarrow 0$; the others correspond to relabelling the x, y and z axes of D_2 (Koster's C_2 axis is z).

7. Conclusions

The existence of the orientation phases clarifies the speculations of Butler and Wybourne (1976a). The phase choices discussed there have no effect on the orientation of the group—changing them merely changes the phases of the partners. (In the presence of branching multiplicity this phase becomes a unitary matrix.) Equation (4.13) shows that a change in orientation phase mixes irreps of the group, i.e. the groups are no longer identical, merely isomorphic. Properties of transformations between bases chosen with respect to isomorphic subgroups of a symmetric group have been studied by Sullivan (1978).

In some applications it is important to know where the symmetry axes lie for the given set of point-group j and jm symbols. Sections 4 and 5 showed how to find such axes, and, further, indicated how these may be rotated, either by changing the orientation phase, or by rotating all partners.

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APPENDIX 2

3jm and 6j tables for some bases of SU_6 and SU_3

To be submitted to J Phys A: Math. Gen. (with R P Bickerstaff, P H Butler, M B Butts and R W Hasse).

Tables 3-10 are not included because the computer type-setting was still being finalized at the time of submission.

3jm and 6j tables for some bases of SU_6 and SU_3

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Short title: 3jm and 6j tables for SU_6 and SU_3

Inspec number: 02:20

ABSTRACT

Tables of 6j symbols for SU_6 and SU_3 and tables of 3jm factors for $SU_6 \supset SU_2 \times SU_3$, $SU_3 \supset U_1 \times SU_2$ and $SU_3 \supset SO_3$ are presented. The tables are computer produced, using a program that implements the building up principle in a general form. Our tables are useful for calculations in high energy, in nuclear, and in solid state physics. Some other tabulations contain errors, and none use all the symmetries available. The n-independence of our SU_n results is discussed by using the various symmetric group-unitary group duality relations.

(1) Introduction

It was recognized long ago (Wigner 1931) that the quantum theory of angular momentum is intimately related to the three-dimensional rotation group. Many aspects of this theory may be generalized to other groups. Griffith (1961) and Koster et al. (1963) calculated coupling coefficients for point groups, which have many applications in solid state and molecular physics calculations. Racah's (1949) work on fractional parentage coefficients (cfp) showed that groups larger than SO_3 are useful for classifying and constructing atomic states and much use has been made of these methods in nuclear theory. More recently SU_3 and other unitary groups have been applied to hadron model calculations.

The highly symmetric 3jm and 6j symbols introduced by Wigner (1940) have many advantages over the less symmetric coupling and recoupling coefficients calculated by Griffith (1961) and Koster et al. (1963) for point groups, de Swart (1963) for SU_3 and Cook and Murtaza (1965), Schülke (1965) and Carter et al (1965) for SU_6. The calculation of the coefficients is greatly simplified, the tabulation is much more compact and the various applications involve the use of more symmetrical equations. 3jms and 6js can be defined for any group (Derome and Sharp 1965, Butler 1975) but many authors still calculate unsymmetrized coefficients. For example Akiyama and Draayer (1973) and Draayer and Akiyama (1973) for SU_3, and So and Strottman (1979) for SU_6.

Several methods have been used to calculate 3jms and 6js (or coupling and recoupling coefficients). These include

projection-operator construction of states, this often involves a transformation from a known basis (such as Akiyama and Draayer's construction of the $SU_3 \supset SO_3$ basis from the $SU_3 \supset U_1 \times SU_2$ basis), ladder operator techniques, which make use of matrix elements and generators (the usual angular momentum approach) and the building up method we use here. The building up process was shown by Butler and Wybourne (1976) to have the advantage of requiring only a knowledge of character theory, chiefly product and branching rules. This is particularly useful for groups with irreps of large dimension such as E_7 (Butler, Haase and Wybourne 1978, 1979) where the other methods are impractical because they involve the construction of very large matrices.

The unitary groups, especially SU_3 and SU_6, have been used extensively since Jahn's (1950) extension of Racah's (1949) cfp work. Harmonic oscillator calculations involve SU_3 (Wybourne 1974, Ch 20), and SU_3 and SU_6 occur in particle physics, particularly in the application of the Wigner-Eckart theorem to the colour hyperfine interaction. Some of the tables presented here have been used by Bickerstaff and Wybourne (1980, 1981) and Black and Wybourne (1981) for multiquark hadron calculations. Likewise, crystal field calculations in the 'strong-field' parentage scheme (Tanabe and Sugano 1954a, 1954b, 1956, Kustov 1977) use the $SU_6 \supset SU_2 \times SU_3$ and $SU_3 \supset SO_3$ bases. Some previous tabulations contain errors and none display all known symmetries. Further, there is the vexing problem of consistency between various tables (for a discussion see Bickerstaff 1981). We

present tablulations of 6j symbols for SU_3 and SU_6 and 3jm factors for $SU_6 \supset SU_2 \times SU_3$, $SU_3 \supset U_1 \times SU_2$ and $SU_3 \supset SO_3$ which are consistent with our 6j tables and the standard SU_2 tables of Rotenberg et al (1959). So and Strottman's (1979) tables for U_6 are not applicable to SU_6 because their phase prescription results in different phases for coefficients which are equivalent under SU_6, while Hogaasen and Sorba (1978) contains normalization errors. Kustov's (1977) SU_6 and SU_3 tables contain errors because he has overlooked the question of product multiplicity in SU_3. Our values are given as exact complex numbers rather than the floating-point values used in Akiyama and Draayer's (1973) calculations for SU_3.

(2) The building up method of calculation

The theory of the generalized Racah-Wigner algebra has been given by Derome and Sharp (1965) and Butler (1975). Butler and Wybourne (1976) recognized that sufficient recursion relations exist in the algebra to allow the calculation of 6j symbols and then 3jm factors, up to the phase and multiplicity freedoms allowed by Schur's lemmas. This building up process was used by Butler (1981) to generate tables for all point-groups.

The continuous groups we consider here have an infinite number of irreps. In the absence of analytic formulae (such as Racah's 1942 formulae for SO_3 and $SO_3 \supset SO_2$) we are restricted to calculating a finite number of 6j symbols and 3jm factors. In deciding which symbols to include, the concept of power is used. We choose a faithful irrep, ε (the irrep{1}for SU_3 and SU_6), and call it the primitive.

The power of λ is defined to be the smallest p for which $(\varepsilon + \varepsilon^*)^p \supset \lambda$. The building-up method may be used to calculate all 6j symbols and 3jm factors up to a certain power: our tables include all irreps up to power 3 in SU_3 and SU_6.

All the groups we consider are quasiambivalent and no non-simple phase irreps occur in the 6js and 3jms we have calculated (see Butler 1975 for a definition of these terms). SU_3 has no non-simple phase irreps (Derome 1967) and the first known non-simple phase irrep of SU_6 is $\{432^21\}$ which is power 6 (Butler and King 1974). Because of these simplifications the equations and the symmetries of Butler 1975 may be simplified to those of the point groups (see Butler 1981 and section 3). We stress that tables which fail, via their phase choices, to employ all possible symmetries require more complicated equations. The choice that Derome and Sharp's (1965) A matrix is unity forces some 6j and 3jm values to be imaginary. It is known that even without this choice some 3jm factors for some imbeddings are always complex. Butler (1980, 1981) gives a simple example for $T \supset D_2$.

Butler (1981) and Bickerstaff and Wybourne (1981) have given a detailed account of the phase and multiplicity freedoms in the 6j symbols and 3jm factors. Phase choices analogous to Reid and Butler's (1980) 'orientation' choices occur in each of the 3jm factor tables presented here. The distinguishing feature of an orientation choice is that the transformation between two sets of 3jm factors with different orientation choices requires primitive transformation factors which are not unity. For point groups this restriction is equivalent to a rotation of the axes.

Some choices of multiplicity separation lead to large prime numbers appearing in the tables. Our choices are based on the ad hoc requirement that numbers should be as simple as possible. Butler and Ford (1979) used a special symmetry of the octahedral group to simplify the numerical values of the 6j symbols for that group but no such symmetries exist for SU_3 or SU_6.

3. Guide to the tables

The 6j and 3jm tables were calculated by the computer program which generated the point group tables of Butler (1981). The tables are computer typeset to preserve accuracy.

Schur-function notation (namely partitions) is used to label irreps (Wybourne 1970, 1974). For U_1 both positive and negative integers occur. The spin covering group of SO_3 is SU_2 and so one has a choice of labelling: either integers and half-integers, j, for SO_3, or integers k for SU_2, where $k = 2j$. Symbols of SO_3 (and therefore for SU_2) are tabulated by Rotenberg, Bivins, Metropolis and Wooten (1959). They include the 3jm factors for $SO_3 \supset SO_2$ ($SU_2 \supset U_1$) under the name "3j symbols". For our table $SU_3 \supset SO_3$ we use the SO_3 labels, while for $SU_3 \supset U_1 \times SU_2$ and $SU_6 \supset SU_2 \times SU_3$ we use the SU_2 labels.

Table 1 lists the irreps of SU_3, up to power 3, giving complex conjugation properties and dimensions. Table 2 contains similar information for SU_6.

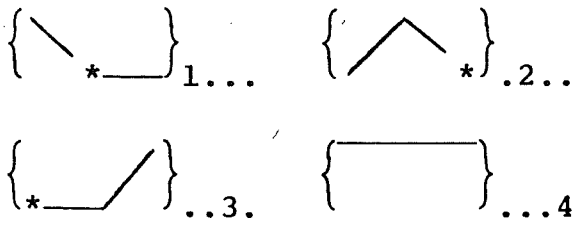
The Kronecker product rules are specified by means of triads. If $\lambda_1 \times \lambda_2 \supset \lambda_3^*$ then $\lambda_1 \times \lambda_2 \times \lambda_3 \supset 0$, where 0 is the identity irrep and * denotes complex conjugation. A triad is the set of three irrep labels, λ_1, λ_2 and λ_3,

together with a multiplicity index r. The r lables any multiple occurence of the identity irrep. The triad structure of SO_3 is well known, but the SO_2 structure of the "3j symbols" is often ignored: If three irreps m_1 m_2 m_3 of U_1 (or SO_2) are to form a triad (multiplicity zero only) then $m_1 + m_2 + m_3 = 0$. All 6j symbols of U_1(and SO_2) are chosen to be +1. Each triad has an associated phase, the 3j phase, which gives the symmetry on reordering coupled products. All relevant 3j's, $\{\lambda_1\ \lambda_2\ \lambda_3\ r\}$ are tabulated at the beginning of the 6j table. (Table 3 for SU_3 and Table 4 for SU_6). For SO_3 one has $\{j_1\ j_2 j_3\ 0\} = (-1)^{j_1+j_2+j_3}$.

The 6j symbol is related to recouplings between a set of six irreps, by means of four couplings. The triads occur in the 6j

$$\left\{\begin{matrix}\lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3\end{matrix}\right\}_{r_1 r_2 r_3 r_4}$$

in the order



Symmetries are used to reduce the size of the tables. The full symmetries are given by Butler (1981) and Butler and Wybourne (1976) but to find a 6j in the tables one only needs the following: The 6j symbols are invariant under even permutations of the columns; there is the complex conjugation symmetry;

$$\left\{\begin{matrix}\lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3\end{matrix}\right\}_{r_1 r_2 r_3 r_4} = \left\{\begin{matrix}\lambda_1^* & \lambda_2^* & \lambda_3^* \\ \mu_1^* & \mu_2^* & \mu_3^*\end{matrix}\right\}^*_{r_1 r_2 r_3 r_4} \tag{3.1}$$

the row flip symmetries, the (23) flip being;

$$= \left\{\begin{matrix}\lambda_1^* & \mu_2 & \mu_3^* \\ \mu_1^* & \lambda_2 & \lambda_3^*\end{matrix}\right\}_{r_4 r_3 r_2 r_1} \tag{3.2}$$

and the column interchange symmetries, the (12) operatiion being

$$= \pm \left\{\begin{matrix}\lambda_2 & \lambda_1 & \lambda_3 \\ \mu_2^* & \mu_1^* & \mu_3^*\end{matrix}\right\}_{r_2 r_1 r_3 r_4} \tag{3.3}$$

The sign $\pm$ is the same for all interchanges and is given in the tables immediately after the multiplicity indices.

In tables 3 and 4, the bold typeface headings denote the top line of the 6j symbol and each subsequent entry denotes a lower line (three irreps, four multiplicity labels), the interchange sign, and the value.

The branching rules are given in tables 5,7 and 9. No branching multiplicity occurs for the cases considered. The tables include the sign of the corresponding 2jm. This is always +1 for $SU_3 \supset SO_3$ and for $SU_6 \supset SU_2 \times SU_3$, while for $SU_3 \supset U_1 \times SU_2$ the orthogonal nature of some SU_3 irreps and the symplectic nature of some SU_2 irreps means that many 2jms are -1. From Table 7, line 6 we have

$$\begin{pmatrix}21 \\ 0.0\end{pmatrix} = \begin{pmatrix}21 \\ 3.1\end{pmatrix} = \begin{pmatrix}21 \\ 0.2\end{pmatrix} = 1 \text{ and } \begin{pmatrix}21 \\ -3.1\end{pmatrix} = -1 \tag{3.4}$$

3jm factors are zero unless the top and bottom rows are traids of the group and subgroups respectively, and unless the columns obey the branching rules. The symmetries of the 3jm are: invariance under cyclic permutations of the columns; a possible sign change for a column interchange, the (12) interchange being;

$$\begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \rho_1 & \rho_2 & \rho_3 \end{pmatrix}^r_s = \pm \begin{pmatrix} \lambda_2 & \lambda_1 & \lambda_3 \\ \rho_2 & \rho_1 & \rho_3 \end{pmatrix} \tag{3.5}$$

and a possible sign change under the complex conjugation symmetry

$$= \pm \begin{pmatrix} \lambda_1^* & \lambda_2^* & \lambda_3^* \\ \rho_1^* & \rho_2^* & \rho_3^* \end{pmatrix}^{r*}_s \tag{3.6}$$

For $SU_3 \supset U_1 \times SU_2$ and $SU_6 \supset SU_2 \times SU_3$ the irrep labels for the direct product subgroup are a product of the labels for each group, and for the second case, the subgroup coupling multiplicity label refers to the multiplicity in SU_3.

The 3jm tables (Tables 6,8, and 10) use the top row of a 3jm as a bold typeface header, each subsequent entry giving the subgroup irrep label pairs, the label s (for Table 10 only), the column interchange sign (for eq 3.5), a star if complex conjugation introduces a negative sign (for eq 3.6), and then the value. The symmetries are used to reduce the size of the tables, the irreps appear in the order of Tables 1 and 2.

Table 1: Irreps of SU_3

Irrep	0	1	1^2	2	2^2	21	3	3^2	31	32
Complex Conjugate	0	1^2	1	2^2	2	21	3^2	3	32	31
Dimension	1	3	3	6	6	8	10	10	15	15

Table 2: Irreps of SU_6

Irrep	0	1	1^5	1^2	1^4	2	2^5	21^4	1^3	21	$2^4 1$	21^3	$2^2 1^3$	3	3^5	31^4	32^4
Complex Conjugate	0	1^5	1	1^4	1^2	2^5	2	21^4	1^3	$2^4 1$	21	$2^2 1^3$	21^3	3^5	3	32^4	31^4
Dimension	1	6	6	15	15	21	21	35	20	70	70	84	84	56	56	120	120

(4) The symmetric group-unitary group duality

The relationship between the structures of the symmetric and unitary groups was recognised by Frobenius and Schur. Weyl (1946) makes much use of this duality, showing that irreps of the unitary groups can be obtained using Young symmetrizers. Both the symmetric and unitary group characters are specified by Schur functions (Littlewood 1950), which were studied by Jacobi, Trudi, Kostka and others long before Schur (1901) showed the connection with the characters of these groups. The use of the purely functional combinatoric properties of Schur-functions has recently proved fruitful in obtaining new identities and thus new computational techniques for character theory (see for example Butler and King 1973a,b, King 1970, 1975, Wybourne 1970). The algebra of Schur-functions makes the dual structures of the characters of S_ℓ and U_n apparent.

The duality goes further than character theory, and one can establish many identities between the Racah-Wigner algebra of S_ℓ and that of U_n. Nuclear shell model theorists used this duality to compute jm and j symbols of U_n (Jahn 1954, Elliott, Hope and Jahn 1953, Kaplan 1962 a,b Horie 1964, Vanagas 1971). Kramer (1967, 1968) obtained the equality of "f-symbols" for symmetric group chains with j symbols of all unitary groups and jm factors in $U_{p+q} \supset U_p U_p$ basis. These results yield the Regge symmetries for the 3jm symbols of $SU_2 \supset U_1$ (Kramer and Seligamn 1969a).

Another approach to duality applies the concept of double coset (DC) generators (Kramer and Seligman 1969b) to relate the matrix elements of double coset generators (DCME) to 9f symbols of a certain symmetric groups chain and hence to appropriate 9j symbols of any unitary group. Sullivan (1976, 1980, and references therein) has formulated the general problem of DC decompositions and arrived at more duality results.

None of these calculations are complete because phase and multiplicity relationships between different unitary and symmetric groups have been left unspecified. In addition, simplifications can be obtained by using the isomorphism between U_n and $U_1 \times SU_n$. The coefficients of U_n calculated by Baird and Biedenharn (1964) and So and Strottman (1979) are not factorizable into $U_1 \times SU_n$ coefficients. The application of the tilde symmetry for S_ℓ (see Butler and Ford 1979) provides further symmetries for U_n coefficients, in analogy to the SU_2 Regge symmetries. A full discussion of these symmetries must include duality phases.

Although the phase questions remain unsolved, our tables provide illustrations of the dualities. The SU_6 6j $\left\{\begin{matrix} 21 & 2^5 & 1^5 \\ 1 & 2 & 1^5 \end{matrix}\right\}$ may be found in table 4, as $\frac{1}{2.3.7}$. Using the 6j symmetries, in particular (13) column interchange and complex conjugation, this becomes

$$\left|\left\{\begin{matrix} 21 & 2^5 & 1^5 \\ 1 & 2 & 1^5 \end{matrix}\right\}_{SU_6}\right| = \left|\left\{\begin{matrix} 1 & 2 & 21^* \\ 1^* & 2 & 1 \end{matrix}\right\}_{SU_6}\right|$$

Writing this as a recoupling coefficient (Butler and Wybourne

1976, eq 13 - note that there is an error in the ordering of subscripts in the 6j symbol on the right hand side of this equation) and using Kramer (1967, eq 6.14) allows us to change unitary groups. From the SU_3 6j table we have

$$= \frac{|2|_{SU_3}}{|2|_{SU_6}} \left| \begin{Bmatrix} 1 & 2 & 21^* \\ 1^* & 2 & 1 \end{Bmatrix}_{SU_3} \right| = \frac{6}{21} \left| \begin{Bmatrix} 21 & 2 & 1 \\ 1^2 & 2^* & 1 \end{Bmatrix}_{SU_3} \right| = \frac{6}{21} \cdot \frac{1}{2.6}$$

while from the SU_2 table, (Rotenberg et al, 1959) this is also

$$= \frac{|2|_{SU_2}}{|2|_{SU_6}} \left| \begin{Bmatrix} 1 & 2 & 21^* \\ 1^* & 2 & 1 \end{Bmatrix}_{SU_2} \right| = \frac{3}{21} \left| \begin{Bmatrix} 1 & 2 & 1 \\ 1 & 2 & 1 \end{Bmatrix}_{SU_2} \right| = \frac{3}{21} \cdot \frac{1}{2.3}$$

In a similar fashion the coupling (or isoscalar) factors of SU_{pq} in the $SU_p \times SU_q$ basis, are p and q independent, (see for example Sullivan 1980,Chen 1981). The 3jm

$$\begin{pmatrix} 1^3 & 1^2 & 1 \\ 1.21 & 0.2 & 1.1 \end{pmatrix}_{\substack{SU_6 \\ SU_2 \times SU_3}} = \sqrt{\frac{2}{5}}$$

as found in table 10, may be successively transformed into a trivial 3jm of $SU_4 \supset SU_2 \times SU_2$:

$$\left| \begin{pmatrix} 1^3 & 1^2 & 1 \\ 1.21 & 0.2 & 1.1 \end{pmatrix}_{\substack{SU_6 \\ SU_2 \times SU_3}} \right| = \left| \begin{pmatrix} 1 & 1^3 & 1^2 \\ 1.1 & 1.21 & 0.2 \end{pmatrix}_{\substack{SU_6 \\ SU_2 \times SU_3}} \right|$$

$$= \left(\frac{|0|_{SU_2} |2|_{SU_3}}{|1^2|_{SU_6}} \right)^{\frac{1}{2}} \left| \left\langle \begin{matrix} 1 & 1^3 \\ 1.1 & 21.21 \end{matrix} \middle| \begin{matrix} 1^4 \\ 2^2.2^2 \end{matrix} \right\rangle_{U_p \times U_q}^{U_{pq}} \right|$$

$$= \left(\frac{|0|_{SU_2} |2|_{SU_3}}{|1^2|_{SU_6}} \cdot \frac{|0|_{SU_4}}{|0|_{SU_2} |0|_{SU_2}} \right)^{\frac{1}{2}} \left| \begin{pmatrix} 1 & 1^3 & 0 \\ 1.1 & 1.1 & 0.0 \end{pmatrix}_{SU_2 \times SU_2} \right|$$

Trivial 3jms are just a ratio of dimensions, in this case unity.

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APPENDIX 3

NOTATION

The following tables give the correspondence between the notation used in this thesis (see Butler 1981) and that of Koster et al (1963) and Griffith (1961). In the computer printed tables (appendix 5, tables 4.2.1, 4.2.3 and 4.2.4) the labels ^a ≡ $\tilde{a}$, a' ≡ $\frac{a}{2}$ and # ≡ $\sqrt{\ }$ are used.

C_2/C_{2h}

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1
Koster et al	Γ_1	Γ_3	Γ_4	Γ_2

C_4

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2
Koster et al	Γ_1	Γ_5	Γ_6	Γ_3	Γ_4	Γ_8	Γ_7	Γ_2

C_6/C_{3h}

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2	-2
Koster et al	Γ_1	Γ_7	Γ_8	Γ_5	Γ_6	Γ_{12}	Γ_{11}	Γ_3	Γ_2
	$\frac{5}{2}$	$-\frac{5}{2}$	3						
Koster et al	Γ_{10}	Γ_9	Γ_4						

D_2	0	$\frac{1}{2}$	$\tilde{0}$	1	$\tilde{1}$
Koster et al	Γ_1	Γ_5	Γ_3	Γ_2	Γ_4
Griffith	A_1	E'	B_1	B_2	B_3

$D_4/D_{4h}/C_{4v}$

	0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{3}{2}$	2	$\tilde{2}$
Koster et al	Γ_1	Γ_6	Γ_2	Γ_5	Γ_7	Γ_3	Γ_4
Griffith	A_1	E'	A_2	E	E"	B_1	B_2

T

	0	$\frac{1}{2}$	1	$\frac{3}{2}$	$-\frac{3}{2}$	2	-2
Koster et al	Γ_1	Γ_5	Γ_4	Γ_6	Γ_7	Γ_2	Γ_3
Griffith	A_1	E'	T	E"	E"'	E	

O/O_h

	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\tilde{1}$	$\frac{\tilde{1}}{2}$	$\tilde{0}$
Koster et al	Γ_1	Γ_6	Γ_4	Γ_8	Γ_3	Γ_5	Γ_7	Γ_2
Griffith	A_1	E'	T_1	U'	E	T_2	E"	A_2

APPENDIX 4

GROUPS CONTAINING INVERSIONS OR REFLECTIONS

All the 3jm and 6j tables of Butler (1981) are constructed from tables for pure rotation groups. Of the thirty-two crystallographic point groups eleven are pure rotation groups and the rest are either direct product groups of a rotation group and the two element inversion group C_i (e.g. O_h, D_{4h}) or contain reflections and rotations but are isomorphic to a pure rotation group (e.g. $T_d \sim O$, $C_{4v} \sim D_4$). This is explained in detail in Koster et al. (1963) and Hamermesh (1962).

We shall quote the results from Butler (1981) which allow us to do calculations using only the pure rotation tables.

The rotation-inversion groups, G_i are direct product groups: $G_i = C_i \times G$. The "full rotation group" O_3 is also a direct product group $SO_3 \times C_i$. Note that the operators of C_i commute with those of G. The two irreps of C_i are + and - (g and u) and the only triads are (+++0) and (+--0). The 3js are +1 and so all non-zero 6j symbols are +1. Hence the non-zero 6j symbols may be obtained directly from the pure rotation group tables.

The jm symbols for $G_i \supset G$ are unity if triad conditions are satisfied, hence those for $G_i \supset H_i$ may be obtained directly from the tables for $G \supset H$.

For the rotation-reflection groups the j and jm symbols are excactly those of the pure rotation groups which they are

isomorphic to. The only non-trivial imbedding is that of a rotation-inversion group G_i containing a rotation-reflection group $\tilde{G}$ which is isomorphic to G. For instance $O_h \supset T_d$ or $D_{4h} \supset C_{4v}$. This imbedding is not trivial because the branching rules are:

$$\lambda^+(G_i) \to \lambda(\tilde{G})$$

$$\lambda^-(G_i) \to \tilde{\lambda}(G)$$

where

$$\tilde{\lambda} = \lambda \times \tilde{O}$$

where $\tilde{O}$ is a one-dimensional irrep of G (not always the one labelled $\tilde{O}$). Note that Butler and Ford (1979) use a slightly different definition.

Butler (1981) shows that the 3jm factors for $G_i \supset \tilde{G}$ are:

$$\begin{pmatrix} \lambda^+ & \mu^+ & \nu^+ \\ \lambda & \mu & \nu \end{pmatrix}_{s\tilde{G}}^{rG_i} = \delta_{rs}$$

$$\begin{pmatrix} \lambda^- & \mu^- & \nu^+ \\ \tilde{\lambda} & \tilde{\mu} & \nu \end{pmatrix}_s^r = |\lambda|^{\frac{1}{2}}|\mu|^{\frac{1}{2}}\{\mu\}\{\lambda\mu\nu r\}\{\tilde{\mu}\mu^*\tilde{O}\}\begin{Bmatrix} \tilde{\lambda} & \tilde{\mu} & \nu \\ \mu^* & \lambda & \tilde{O} \end{Bmatrix}_{00rs}$$

These formulae were used by the computer program to treat these imbeddings.

When calculating transformation coefficients between the JM basis of O_3 and a point-group basis we use the result that the even states are the same as pure rotation ones and the odd ones are related by:

$$\langle -JM|-J\lambda\mu\tilde{\mu}\tilde{i}\rangle = \langle +JM|+J\lambda\mu\mu i\rangle (-)^{2J}$$

$$\begin{pmatrix} J^*_- & J_+ & O_- \\ \lambda^* & \lambda & O \\ \mu^* & \mu & O \\ \tilde{\mu}^* & \mu & \tilde{O} \\ \tilde{i}^* & i & \tilde{O} \end{pmatrix}^* \begin{pmatrix} J_- \\ \lambda \\ \mu \\ \tilde{\mu} \\ \tilde{\imath} \end{pmatrix} |J|^{\frac{1}{2}}$$

which is derived by expanding the bra and ket on the left hand side in terms of coupling coefficients and J_+ and O_- bras and kets. Note that this phase is not always real, for instance for $O_3 \supset O_h \supset D_{3h} \supset C_{3v} \supset C_3$.

APPENDIX 5: Transformation from $O_3 \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4$ to the JM Basis. The format is: $|O_3 \supset O_h \supset D_{4h} \supset C_{4v} \supset C_4$ ket> $= \Sigma_M |$JM ket> x (transformation coefficient). For notation see appendix 3.

!+ 0 0 0 0 0 > = !+ 0 0 > +1

!+ 1' 1' 1' 1' 1'> = !+ 1' 1'> +1

!+ 1' 1' 1' 1'-1'> = !+ 1'-1'> +1

!+ 1 1 ^0 ^0 0 > = !+ 1 0 > +1

!+ 1 1 1 1 1 > = !+ 1 1 > -1

!+ 1 1 1 1 -1 > = !+ 1 -1 > -1

!+ 3' 3' 1' 1' 1'> = !+ 3' 1'> +1

!+ 3' 3' 1' 1'-1'> = !+ 3'-1'> -1

!+ 3' 3' 3' 3' 3'> = !+ 3' 3'> +1

!+ 3' 3' 3' 3'-3'> = !+ 3'-3'> +1

!+ 2 2 0 0 0 > = !+ 2 0 > -1

!+ 2 2 2 2 2 > = !+ 2 2 > -1/#2 + !+ 2 -2 > -1/#2

!+ 2 ^1 1 1 1 > = !+ 2 1 > -1

!+ 2 ^1 1 1 -1 > = !+ 2 -1 > +1

!+ 2 ^1 ^2 ^2 2 > = !+ 2 2 > +1/#2 + !+ 2 -2 > -1/#2

!+ 5' 3' 1' 1' 1'> = !+ 5' 1'> +1

!+ 5' 3' 1' 1'-1'> = !+ 5'-1'> +1

!+ 5' 3' 3' 3' 3'> = !+ 5' 3'> -1/#2.3 + !+ 5'-5'> -#5/#2.3

!+ 5' 3' 3' 3'-3'> = !+ 5' 5'> +#5/#2.3 + !+ 5'-3'> +1/#2.3

!+ 5'^1' 3' 3' 3'> = !+ 5' 3'> +#5/#2.3 + !+ 5'-5'> -1/#2.3

!+ 5'^1' 3' 3'-3'> = !+ 5' 5'> +1/#2.3 + !+ 5'-3'> -#5/#2.3

!+ 3 1 ^0 ^0 0 > = !+ 3 0 > -1

!+ 3 1 1 1 1 > = !+ 3 1 > -#3/2#2 + !+ 3 -3 > -#5/2#2

!+ 3 1 1 1 -1 > = !+ 3 3 > -#5/2#2 + !+ 3 -1 > -#3/2#2

!+ 3 ^1 1 1 1 > = !+ 3 1 > -#5/2#2 + !+ 3 -3 > +#3/2#2

!+ 3 ^1 1 1 -1 > = !+ 3 3 > +#3/2#2 + !+ 3 -1 > -#5/2#2

!+ 3 ^1 ^2 ^2 2 > = !+ 3 2 > -1/#2 + !+ 3 -2 > -1/#2

!+ 3 ^0 2 2 2 > = !+ 3 2 > -1/#2 + !+ 3 -2 > +1/#2

!+ 7' 1' 1' 1' 1'> = !+ 7' 1'> -#7/2#3 + !+ 7'-7'> -#5/2#3

!+ 7' 1' 1' 1'-1'> = !+ 7' 7'> +#5/2#3 + !+ 7'-1'> +#7/2#3

```
!+ 7' 3' 1' 1' 1'> = !+  7' 1'> -#5/2#3 + !+  7'-7'> +#7/2#3
!+ 7' 3' 1' 1'-1'> = !+  7' 7'> -#7/2#3 + !+  7'-1'> +#5/2#3
!+ 7' 3' 3' 3' 3'> = !+  7' 3'> +#3/2 + !+  7'-5'> +1/2
!+ 7' 3' 3' 3'-3'> = !+  7' 5'> +1/2 + !+  7'-3'> +#3/2
!+ 7'^1' 3' 3' 3'> = !+  7' 3'> +1/2 + !+  7'-5'> -#3/2
!+ 7'^1' 3' 3'-3'> = !+  7' 5'> -#3/2 + !+  7'-3'> +1/2
!+ 4  0  0  0  0 > = !+  4  4 > +#5/2#2.3 + !+  4  0 > +#7/2#3
                   + !+  4 -4 > +#5/2#2.3
!+ 4  1 ^0 ^0  0 > = !+  4  4 > +1/#2 + !+  4 -4 > -1/#2
!+ 4  1  1  1  1 > = !+  4  1 > +#7/2#2 + !+  4 -3 > +1/2#2
!+ 4  1  1  1 -1 > = !+  4  3 > -1/2#2 + !+  4 -1 > -#7/2#2
!+ 4  2  0  0  0 > = !+  4  4 > -#7/2#2.3 + !+  4  0 > +#5/2#3
                   + !+  4 -4 > -#7/2#2.3
!+ 4  2  2  2  2 > = !+  4  2 > -1/#2 + !+  4 -2 > -1/#2
!+ 4 ^1  1  1  1 > = !+  4  1 > +1/2#2 + !+  4 -3 > -#7/2#2
!+ 4 ^1  1  1 -1 > = !+  4  3 > +#7/2#2 + !+  4 -1 > -1/2#2
!+ 4 ^1 ^2 ^2  2 > = !+  4  2 > +1/#2 + !+  4 -2 > -1/#2
!+ 9' 1' 1' 1' 1'> = !+  9' 9'> +#3/2#2 + !+  9' 1'> +#7/2#3 + !+  9'-7'> +1/2#2.3
!+ 9' 1' 1' 1'-1'> = !+  9' 7'> +1/2#2.3 + !+  9'-1'> +#7/2#3 + !+  9'-9'> +#3/2#2
!+ 9'(0) 3' 1' 1' 1'> = !+  9' 9'> +1/#2.5 + !+  9'-7'> -3/#2.5
!+ 9'(0) 3' 1' 1'-1'> = !+  9' 7'> -3/#2.5 + !+  9'-9'> +1/#2.5
!+ 9'(0) 3' 3' 3' 3'> = !+  9' 3'> -#7/#2.5 + !+  9'-5'> +#3/#2.5
!+ 9'(0) 3' 3' 3'-3'> = !+  9' 5'> -#3/#2.5 + !+  9'-3'> +#7/#2.5
!+ 9'(1) 3' 1' 1' 1'> = !+  9' 9'> +#3.7/2#2.5 + !+  9' 1'> -#5/2#3
                      + !+  9'-7'> +#7/2#2.3.5
!+ 9'(1) 3' 1' 1'-1'> = !+  9' 7'> +#7/2#2.3.5 + !+  9'-1'> -#5/2#3
                      + !+  9'-9'> +#3.7/2#2.5
!+ 9'(1) 3' 3' 3' 3'> = !+  9' 3'> -#3/#2.5 + !+  9'-5'> -#7/#2.5
!+ 9'(1) 3' 3' 3'-3'> = !+  9' 5'> +#7/#2.5 + !+  9'-3'> +#3/#2.5
!+ 5 (0) 1 ^0 ^0  0 > = !+  5  4 > -#5.7/2#2.11 + !+  5  0 > +3/2#11
                      + !+  5 -4 > -#5.7/2#2.11
!+ 5 (0) 1  1  1  1 > = !+  5  5 > -#7/4#2.11 + !+  5  1 > +#3.5/4#11
                      + !+  5 -3 > -3#5.7/4#2.11
!+ 5 (0) 1  1  1 -1 > = !+  5  3 > -3#5.7/4#2.11 + !+  5 -1 > +#3.5/4#11
                      + !+  5 -5 > -#7/4#2.11
!+ 5 (1) 1 ^0 ^0  0 > = !+  5  4 > +3/2#2.11 + !+  5  0 > +#5.7/2#11
                      + !+  5 -4 > +3/2#2.11
```

```
!+ 5 (1) 1  1  1  1 > = !+  5  5 > -3#5/2#2.11 + !+  5  1 > -#3.7/2#11
                       + !+  5 -3 > -1/2#2.11
!+ 5 (1) 1  1  1 -1 > = !+  5  3 > -1/2#2.11 + !+  5 -1 > -#3.7/2#11
                       + !+  5 -5 > -3#5/2#2.11
!+ 5  2  0  0  0 > = !+  5  4 > -1/#2 + !+  5 -4 > +1/#2
!+ 5  2  2  2  2 > = !+  5  2 > +1/#2 + !+  5 -2 > -1/#2
!+ 5 ^1  1  1  1 > = !+  5  5 > -#3.5/4#2 + !+  5  1 > +#7/4 + !+  5 -3 > +#3/4#2
!+ 5 ^1  1  1 -1 > = !+  5  3 > +#3/4#2 + !+  5 -1 > +#7/4 + !+  5 -5 > -#3.5/4#2
!+ 5 ^1 ^2 ^2  2 > = !+  5  2 > -1/#2 + !+  5 -2 > -1/#2
!+11' 1' 1' 1' 1'> = !+ 11' 9'> -#7/4#3 + !+ 11' 1'> +1/2#2 + !+ 11'-7'> -#5.7/4#3
!+11' 1' 1' 1'-1'> = !+ 11' 7'> +#5.7/4#3 + !+ 11'-1'> -1/2#2 + !+ 11'-9'> +#7/4#3
!+11'(0) 3' 1' 1' 1'> = !+ 11' 9'> +19/4#3.11 + !+ 11' 1'> -#7/2#2.11
                       + !+ 11'-7'> -5#5/4#3.11
!+11'(0) 3' 1' 1'-1'> = !+ 11' 7'> +5#5/4#3.11 + !+ 11'-1'> +#7/2#2.11
                       + !+ 11'-9'> -19/4#3.11
!+11'(0) 3' 3' 3' 3'> = !+ 11'11'> -1/4 + !+ 11' 3'> +#3.5/2#2.11
                       + !+ 11'-5'> -3#3.5/4#11
!+11'(0) 3' 3' 3'-3'> = !+ 11' 5'> -3#3.5/4#11 + !+ 11'-3'> +#3.5/2#2.11
                       + !+ 11'-11'> -1/4
!+11'(1) 3' 1' 1' 1'> = !+ 11' 9'> +#3.5/2#2.11 + !+ 11' 1'> +#5.7/2#11
                       + !+ 11'-7'> +#3/2#2.11
!+11'(1) 3' 1' 1'-1'> = !+ 11' 7'> -#3/2#2.11 + !+ 11'-1'> -#5.7/2#11
                       + !+ 11'-9'> -#3.5/2#2.11
!+11'(1) 3' 3' 3' 3'> = !+ 11'11'> +#5/2#2 + !+ 11' 3'> +7/2#3.11
                       + !+ 11'-5'> +1/2#2.3.11
!+11'(1) 3' 3' 3'-3'> = !+ 11' 5'> +1/2#2.3.11 + !+ 11'-3'> +7/2#3.11
                       + !+ 11'-11'> +#5/2#2
!+11'^1' 3' 3' 3'> = !+ 11'11'> +#5/4 + !+ 11' 3'> -#11/2#2.3 + !+ 11'-5'> -#11/4#3
!+11'^1' 3' 3'-3'> = !+ 11' 5'> -#11/4#3 + !+ 11'-3'> -#11/2#2.3
                   + !+ 11'-11'> +#5/4
!+ 6  0  0  0  0 > = !+  6  4 > +#7/4 + !+  6  0 > -1/2#2 + !+  6 -4 > +#7/4
!+ 6  1 ^0 ^0  0 > = !+  6  4 > +1/#2 + !+  6 -4 > -1/#2
!+ 6  1  1  1  1 > = !+  6  5 > +#11/4#2 + !+  6  1 > -#3/4 + !+  6 -3 > +#3.5/4#2
!+ 6  1  1  1 -1 > = !+  6  3 > -#3.5/4#2 + !+  6 -1 > +#3/4 + !+  6 -5 > -#11/4#2
!+ 6  2  0  0  0 > = !+  6  4 > +1/4 + !+  6  0 > +#7/2#2 + !+  6 -4 > +1/4
!+ 6  2  2  2  2 > = !+  6  6 > +#11/4#2 + !+  6  2 > +#5/4#2 + !+  6 -2 > +#5/4#2
                   + !+  6 -6 > +#11/4#2
!+ 6 (0)^1  1  1  1 > = !+  6  5 > +#3.5/4#2.7 + !+  6  1 > -#5.11/4#7
```

```
                        + !+  6 -3 > -3#11/4#2.7
!+ 6 (0)^1  1  1 -1 > = !+  6  3 > +3#11/4#2.7 + !+  6 -1 > +#5.11/4#7
                        + !+  6 -5 > -#3.5/4#2.7
!+ 6 (0)^1 ^2 ^2  2 > = !+  6  6 > +3#5/4#7 + !+  6  2 > -#11/4#7
                        + !+  6 -2 > +#11/4#7 + !+  6 -6 > -3#5/4#7
!+ 6 (1)^1  1  1  1 > = !+  6  5 > -#3.11/2#2.7 + !+  6  1 > -3/2#7
                        + !+  6 -3 > +#5/2#2.7
!+ 6 (1)^1  1  1 -1 > = !+  6  3 > -#5/2#2.7 + !+  6 -1 > +3/2#7
                        + !+  6 -5 > +#3.11/2#2.7
!+ 6 (1)^1 ^2 ^2  2 > = !+  6  6 > +#11/4#7 + !+  6  2 > +3#5/4#7
                        + !+  6 -2 > -3#5/4#7 + !+  6 -6 > -#11/4#7
!+ 6 ^0  2  2  2 > = !+  6  6 > -#5/4#2 + !+  6  2 > +#11/4#2 + !+  6 -2 > +#11/4#2
                    + !+  6 -6 > -#5/4#2
!+13' 1' 1' 1' 1'> = !+ 13' 9'> +#11/4 + !+ 13' 1'> -1/2#2 + !+ 13'-7'> +#3/4
!+13' 1' 1' 1'-1'> = !+ 13' 7'> +#3/4 + !+ 13'-1'> -1/2#2 + !+ 13'-9'> +#11/4
!+13'(0) 3' 1' 1' 1'> = !+ 13' 9'> +1/2#2.7 + !+ 13' 1'> -#11/2#7
                        + !+ 13'-7'> -#3.11/2#2.7
!+13'(0) 3' 1' 1'-1'> = !+ 13' 7'> -#3.11/2#2.7 + !+ 13'-1'> -#11/2#7
                        + !+ 13'-9'> +1/2#2.7
!+13'(0) 3' 3' 3' 3'> = !+ 13'11'> -1/#7 + !+ 13' 3'> +#11/2#7
                        + !+ 13'-13'> +#13/2#7
!+13'(0) 3' 3' 3'-3'> = !+ 13'13'> -#13/2#7 + !+ 13'-3'> -#11/2#7
                        + !+ 13'-11'> +1/#7
!+13'(1) 3' 1' 1' 1'> = !+ 13' 9'> -#3.11/4#7 + !+ 13' 1'> -3#3/2#2.7
                        + !+ 13'-7'> +5/4#7
!+13'(1) 3' 1' 1'-1'> = !+ 13' 7'> +5/4#7 + !+ 13'-1'> -3#3/2#2.7
                        + !+ 13'-9'> -#3.11/4#7
!+13'(1) 3' 3' 3' 3'> = !+ 13'11'> +5#11/4#2.3.7 + !+ 13' 3'> -#3/4#2.7
                        + !+ 13'-5'> +#5.7/4#2.3 + !+ 13'-13'> +#11.13/4#2.3.7
!+13'(1) 3' 3' 3'-3'> = !+ 13'13'> -#11.13/4#2.3.7 + !+ 13' 5'> -#5.7/4#2.3
                        + !+ 13'-3'> +#3/4#2.7 + !+ 13'-11'> -5#11/4#2.3.7
!+13'(0)^1' 3' 3' 3'> = !+ 13'11'> -#5/4#2.7 + !+ 13' 3'> +#5.11/4#2.7
                        + !+ 13'-5'> +3#11/4#2.7 + !+ 13'-13'> -#5.13/4#2.7
!+13'(0)^1' 3' 3'-3'> = !+ 13'13'> +#5.13/4#2.7 + !+ 13' 5'> -3#11/4#2.7
                        + !+ 13'-3'> -#5.11/4#2.7 + !+ 13'-11'> +#5/4#2.7
!+13'(1)^1' 3' 3' 3'> = !+ 13'11'> +#11.13/4#3.7 + !+ 13' 3'> +#3.13/4#7
                        + !+ 13'-5'> -#5.13/4#3.7 + !+ 13'-13'> -#11/4#3.7
!+13'(1)^1' 3' 3'-3'> = !+ 13'13'> +#11/4#3.7 + !+ 13' 5'> +#5.13/4#3.7
                        + !+ 13'-3'> -#3.13/4#7 + !+ 13'-11'> -#11.13/4#3.7
```

```
!+ 7 (0) 1 ^0 ^0  0 > = !+  7  4 > +#3.11/4#5 + !+  7  0 > -#7/2#2.5
                      + !+  7 -4 > +#3.11/4#5
!+ 7 (0) 1  1  1  1 > = !+  7  5 > -#3.11/2#2.5 + !+  7  1 > +1/#2.5
                      + !+  7 -3 > -#3/2#2.5
!+ 7 (0) 1  1  1 -1 > = !+  7  3 > -#3/2#2.5 + !+  7 -1 > +1/#2.5
                      + !+  7 -5 > -#3.11/2#2.5
!+ 7 (1) 1 ^0 ^0  0 > = !+  7  4 > +#7/4#5 + !+  7  0 > +#3.11/2#2.5
                      + !+  7 -4 > +#7/4#5
!+ 7 (1) 1  1  1  1 > = !+  7  5 > +#7/8#2.5 + !+  7  1 > +#3.7.11/8#2.5
                      + !+  7 -3 > +#7.11/8#2.5 + !+  7 -7 > +#5.13/8#2
!+ 7 (1) 1  1  1 -1 > = !+  7  7 > +#5.13/8#2 + !+  7  3 > +#7.11/8#2.5
                      + !+  7 -1 > +#3.7.11/8#2.5 + !+  7 -5 > +#7/8#2.5
!+ 7  2  0  0  0 > = !+  7  4 > -1/#2 + !+  7 -4 > +1/#2
!+ 7  2  2  2  2 > = !+  7  6 > +#13/4#3 + !+  7  2 > -#11/4#3
                    + !+  7 -2 > +#11/4#3 + !+  7 -6 > -#13/4#3
!+ 7 (0)^1  1  1  1 > = !+  7  5 > -1/4#2.7 + !+  7  1 > +#3.11/4#2.7
                      + !+  7 -3 > +3#11/4#2.7 + !+  7 -7 > -#13/4#2
!+ 7 (0)^1  1  1 -1 > = !+  7  7 > -#13/4#2 + !+  7  3 > +3#11/4#2.7
                      + !+  7 -1 > +#3.11/4#2.7 + !+  7 -5 > -1/4#2.7
!+ 7 (0)^1 ^2 ^2  2 > = !+  7  6 > -#13/4#2.7 + !+  7  2 > +3#11/4#2.7
                      + !+  7 -2 > +3#11/4#2.7 + !+  7 -6 > -#13/4#2.7
!+ 7 (1)^1  1  1  1 > = !+  7  5 > +#11.13/8#2.7 + !+  7  1 > +3#3.13/8#2.7
                      + !+  7 -3 > -5#13/8#2.7 + !+  7 -7 > -#11/8#2
!+ 7 (1)^1  1  1 -1 > = !+  7  7 > -#11/8#2 + !+  7  3 > -5#13/8#2.7
                      + !+  7 -1 > +3#3.13/8#2.7 + !+  7 -5 > +#11.13/8#2.7
!+ 7 (1)^1 ^2 ^2  2 > = !+  7  6 > +3#11/4#2.7 + !+  7  2 > +#13/4#2.7
                      + !+  7 -2 > +#13/4#2.7 + !+  7 -6 > +3#11/4#2.7
!+ 7 ^0  2  2  2 > = !+  7  6 > -#11/4#3 + !+  7  2 > -#13/4#3
                    + !+  7 -2 > +#13/4#3 + !+  7 -6 > +#11/4#3
!+15' 1' 1' 1' 1'> = !+ 15' 9'> +#7/8#3 + !+ 15' 1'> +#3.11/8 + !+ 15'-7'> +#7/8
                    + !+ 15'-15'> +#5.13/8#3
!+15' 1' 1' 1'-1'> = !+ 15'15'> -#5.13/8#3 + !+ 15' 7'> -#7/8 + !+ 15'-1'> -#3.11/8
                    + !+ 15'-9'> -#7/8#3
!+15'(0) 3' 1' 1' 1'> = !+ 15' 9'> +3#11/4#2.5 + !+ 15' 1'> -#7/2#2.5
                      + !+ 15'-7'> +#3.11/4#2.5
!+15'(0) 3' 1' 1'-1'> = !+ 15' 7'> -#3.11/4#2.5 + !+ 15'-1'> +#7/2#2.5
```

```
                        + !+ 15'-9'> -3#11/4#2.5
!+15'(0) 3' 3' 3' 3'> = !+ 15'11'> +#11.13/4#2.5 + !+ 15' 3'> -#3/2#2.5
                        + !+ 15'-5'> +1/4#2
!+15'(0) 3' 3' 3'-3'> = !+ 15' 5'> +1/4#2 + !+ 15'-3'> -#3/2#2.5
                        + !+ 15'-11'> +#11.13/4#2.5
!+15'(1) 3' 1' 1' 1'> = !+ 15' 9'> +7#7/8.3#5 + !+ 15' 1'> +3#11/8#5
                        + !+ 15'-7'> -#7/8#3.5 + !+ 15'-15'> -5#13/8.3
!+15'(1) 3' 1' 1'-1'> = !+ 15'15'> +5#13/8.3 + !+ 15' 7'> +#7/8#3.5
                        + !+ 15'-1'> -3#11/8#5 + !+ 15'-9'> -7#7/8.3#5
!+15'(1) 3' 3' 3' 3'> = !+ 15'11'> -#7.13/8.3#5 + !+ 15' 3'> -#3.7.11/8#5
                        + !+ 15'-5'> -#7.11/8.3 + !+ 15'-13'> -#5.13/8.3
!+15'(1) 3' 3' 3'-3'> = !+ 15'13'> -#5.13/8.3 + !+ 15' 5'> -#7.11/8.3
                        + !+ 15'-3'> -#3.7.11/8#5 + !+ 15'-11'> -#7.13/8.3#5
!+15'(2) 3' 1' 1' 1'> = !+ 15' 9'> +#5.13/4.3#2 + !+ 15'-7'> -#5.13/4#2.3
                        + !+ 15'-15'> +#7/2.3#2
!+15'(2) 3' 1' 1'-1'> = !+ 15'15'> -#7/2.3#2 + !+ 15' 7'> +#5.13/4#2.3
                        + !+ 15'-9'> -#5.13/4.3#2
!+15'(2) 3' 3' 3' 3'> = !+ 15'11'> -#5/4.3#2 + !+ 15'-5'> +#11.13/4.3#2
                        + !+ 15'-13'> -#5.7/2.3#2
!+15'(2) 3' 3' 3'-3'> = !+ 15'13'> -#5.7/2.3#2 + !+ 15' 5'> +#11.13/4.3#2
                        + !+ 15'-11'> -#5/4.3#2
!+15'^1' 3' 3' 3'> = !+ 15'11'> -#11/8#3 + !+ 15' 3'> -#13/8
                     + !+ 15'-5'> +#5.13/8#3 + !+ 15'-13'> +#7.11/8#3
!+15'^1' 3' 3'-3'> = !+ 15'13'> +#7.11/8#3 + !+ 15' 5'> +#5.13/8#3
                     + !+ 15'-3'> -#13/8 + !+ 15'-11'> -#11/8#3
!+ 8  0  0  0  0 > = !+  8  8 > -#5.13/8#2.3 + !+  8  4 > -#7/4#2.3
                     + !+  8  0 > -#3.11/8 + !+  8 -4 > -#7/4#2.3
                     + !+  8 -8 > -#5.13/8#2.3
!+ 8 (0) 1 ^0 ^0  0 > = !+  8  8 > -#5.13/4.3 + !+  8  4 > -#7/4.3
                        + !+  8 -4 > +#7/4.3 + !+  8 -8 > +#5.13/4.3
!+ 8 (0) 1  1  1  1 > = !+  8  5 > -#7.13/8.3#2 + !+  8  1 > -3#11/8#2
                        + !+  8 -3 > -#5.7/8#2.3 + !+  8 -7 > -#5.13/8.3#2
!+ 8 (0) 1  1  1 -1 > = !+  8  7 > +#5.13/8.3#2 + !+  8  3 > +#5.7/8#2.3
                        + !+  8 -1 > +3#11/8#2 + !+  8 -5 > +#7.13/8.3#2
!+ 8 (1) 1 ^0 ^0  0 > = !+  8  8 > +#7/4.3 + !+  8  4 > -#5.13/4.3
                        + !+  8 -4 > +#5.13/4.3 + !+  8 -8 > -#7/4.3
!+ 8 (1) 1  1  1  1 > = !+  8  5 > -#5/2.3#2 + !+  8 -3 > +#13/2#2.3
                        + !+  8 -7 > -#7/3#2
```

```
!+ 8 (1) 1  1  1 -1 > = !+  8  7 > +#7/3#2 + !+  8  3 > -#13/2#2.3
                       + !+  8 -5 > +#5/2.3#2
!+ 8 (0) 2  0  0  0 > = !+  8  8 > +#7.11.13/8.4#3 + !+  8  4 > -#5.11/8.2#3
                       + !+  8  0 > -#3.5.7/8.2#2 + !+  8 -4 > -#5.11/8.2#3
                       + !+  8 -8 > +#7.11.13/8.4#3
!+ 8 (0) 2  2  2  2 > = !+  8  2 > +1/#2 + !+  8 -2 > +1/#2
!+ 8 (1) 2  0  0  0 > = !+  8  8 > -#5/8.4 + !+  8  4 > -#7.13/8.2
                       + !+  8  0 > +#11.13/8.2#2 + !+  8 -4 > -#7.13/8.2
                       + !+  8 -8 > -#5/8.4
!+ 8 (1) 2  2  2  2 > = !+  8  6 > -1/#2 + !+  8 -6 > -1/#2
!+ 8 (0)^1  1  1  1 > = !+  8  5 > -#3.11/8#2.17 + !+  8  1 > -#3.7.13/8#2.17
                       + !+  8 -3 > +#5.11.13/8#2.17 + !+  8 -7 > +#3.5.7.11/8#2.17
!+ 8 (0)^1  1  1 -1 > = !+  8  7 > -#3.5.7.11/8#2.17 + !+  8  3 > -#5.11.13/8#2.17
                       + !+  8 -1 > +#3.7.13/8#2.17 + !+  8 -5 > +#3.11/8#2.17
!+ 8 (0)^1 ^2 ^2  2 > = !+  8  6 > -#7.11/4#2.17 + !+  8  2 > -#3.5.13/4#2.17
                       + !+  8 -2 > +#3.5.13/4#2.17 + !+  8 -6 > +#7.11/4#2.17
!+ 8 (1)^1  1  1  1 > = !+  8  5 > -#5.7.13/4#2.17 + !+  8  1 > +#5.11/4#2.17
                       + !+  8 -3 > -#3.7/4#2.17 + !+  8 -7 > +#13/4#2.17
!+ 8 (1)^1  1  1 -1 > = !+  8  7 > -#13/4#2.17 + !+  8  3 > +#3.7/4#2.17
                       + !+  8 -1 > -#5.11/4#2.17 + !+  8 -5 > +#5.7.13/4#2.17
!+ 8 (1)^1 ^2 ^2  2 > = !+  8  6 > +#3.5.13/4#2.17 + !+  8  2 > -#7.11/4#2.17
                       + !+  8 -2 > +#7.11/4#2.17 + !+  8 -6 > -#3.5.13/4#2.17
ODD ONES START HERE
!- 0  0  0 ^0  0 > = !-  0  0 > +1
!- 1' 1' 1' 1' 1'> = !-  1' 1'> -1
!- 1' 1' 1' 1'-1'> = !-  1'-1'> +1
!- 1  1 ^0  0  0 > = !-  1  0 > -1
!- 1  1  1  1  1 > = !-  1  1 > +1
!- 1  1  1  1 -1 > = !-  1 -1 > -1
!- 3' 3' 1' 1' 1'> = !-  3' 1'> -1
!- 3' 3' 1' 1'-1'> = !-  3'-1'> -1
!- 3' 3' 3' 3' 3'> = !-  3' 3'> -1
!- 3' 3' 3' 3'-3'> = !-  3'-3'> +1
!- 2  2  0 ^0  0 > = !-  2  0 > -1
!- 2  2  2 ^2  2 > = !-  2  2 > -1/#2 + !-  2 -2 > -1/#2
!- 2 ^1  1  1  1 > = !-  2  1 > +1
!- 2 ^1  1  1 -1 > = !-  2 -1 > +1
!- 2 ^1 ^2                    2 + !-  2 -2 > -1/#2
```

```
!- 5' 3' 1' 1' 1'> = !-  5' 1'> -1
!- 5' 3' 1' 1'-1'> = !-  5'-1'> +1
!- 5' 3' 3' 3' 3'> = !-  5' 3'> +1/#2.3 + !-  5'-5'> +#5/#2.3
!- 5' 3' 3' 3'-3'> = !-  5' 5'> +#5/#2.3 + !-  5'-3'> +1/#2.3
!- 5'^1' 3' 3' 3'> = !-  5' 3'> -#5/#2.3 + !-  5'-5'> +1/#2.3
!- 5'^1' 3' 3'-3'> = !-  5' 5'> +1/#2.3 + !-  5'-3'> -#5/#2.3
!- 3  1 ^0  0  0 > = !-  3  0 > +1
!- 3  1  1  1  1 > = !-  3  1 > +#3/2#2 + !-  3 -3 > +#5/2#2
!- 3  1  1  1 -1 > = !-  3  3 > -#5/2#2 + !-  3 -1 > -#3/2#2
!- 3 ^1  1  1  1 > = !-  3  1 > +#5/2#2 + !-  3 -3 > -#3/2#2
!- 3 ^1  1  1 -1 > = !-  3  3 > +#3/2#2 + !-  3 -1 > -#5/2#2
!- 3 ^1 ^2  2  2 > = !-  3  2 > -1/#2 + !-  3 -2 > -1/#2
!- 3 ^0  2 ^2  2 > = !-  3  2 > -1/#2 + !-  3 -2 > +1/#2
!- 7' 1' 1' 1' 1'> = !-  7' 1'> +#7/2#3 + !-  7'-7'> +#5/2#3
!- 7' 1' 1' 1'-1'> = !-  7' 7'> +#5/2#3 + !-  7'-1'> +#7/2#3
!- 7' 3' 1' 1' 1'> = !-  7' 1'> +#5/2#3 + !-  7'-7'> -#7/2#3
!- 7' 3' 1' 1'-1'> = !-  7' 7'> -#7/2#3 + !-  7'-1'> +#5/2#3
!- 7' 3' 3' 3' 3'> = !-  7' 3'> -#3/2 + !-  7'-5'> -1/2
!- 7' 3' 3' 3'-3'> = !-  7' 5'> +1/2 + !-  7'-3'> +#3/2
!- 7'^1' 3' 3' 3'> = !-  7' 3'> -1/2 + !-  7'-5'> +#3/2
!- 7'^1' 3' 3'-3'> = !-  7' 5'> -#3/2 + !-  7'-3'> +1/2
!- 4  0  0 ^0  0 > = !-  4  4 > +#5/2#2.3 + !-  4  0 > +#7/2#3
                   + !-  4 -4 > +#5/2#2.3
!- 4  1 ^0  0  0 > = !-  4  4 > -1/#2 + !-  4 -4 > +1/#2
!- 4  1  1  1  1 > = !-  4  1 > -#7/2#2 + !-  4 -3 > -1/2#2
!- 4  1  1  1 -1 > = !-  4  3 > -1/2#2 + !-  4 -1 > -#7/2#2
!- 4  2  0 ^0  0 > = !-  4  4 > -#7/2#2.3 + !-  4  0 > +#5/2#3
                   + !-  4 -4 > -#7/2#2.3
!- 4  2  2 ^2  2 > = !-  4  2 > -1/#2 + !-  4 -2 > -1/#2
!- 4 ^1  1  1  1 > = !-  4  1 > -1/2#2 + !-  4 -3 > +#7/2#2
!- 4 ^1  1  1 -1 > = !-  4  3 > +#7/2#2 + !-  4 -1 > -1/2#2
!- 4 ^1 ^2  2  2 > = !-  4  2 > +1/#2 + !-  4 -2 > -1/#2
!- 9' 1' 1' 1' 1'> = !-  9' 9'> -#3/2#2 + !-  9' 1'> -#7/2#3 + !-  9'-7'> -1/2#2.3
!- 9' 1' 1' 1'-1'> = !-  9' 7'> +1/2#2.3 + !-  9'-1'> +#7/2#3 + !-  9'-9'> +#3/2#2
!- 9'(0) 3' 1' 1' 1'> = !-  9' 9'> -1/#2.5 + !-  9'-7'> +3/#2.5
!- 9'(0) 3' 1' 1'-1'> = !-  9' 7'> -3/#2.5 + !-  9'-9'> +1/#2.5
!- 9'(0) 3' 3' 3' 3'> = !-  9' 3'> +#7/#2.5 + !-  9'-5'> -#3/#2.5
```

```
!- 9'(0) 3' 3' 3'-3'> = !-  9' 5'> -#3/#2.5 + !-  9'-3'> +#7/#2.5
!- 9'(1) 3' 1' 1' 1'> = !-  9' 9'> -#3.7/2#2.5 + !-  9' 1'> +#5/2#3
                       + !-  9'-7'> -#7/2#2.3.5
!- 9'(1) 3' 1' 1'-1'> = !-  9' 7'> +#7/2#2.3.5 + !-  9'-1'> -#5/2#3
                       + !-  9'-9'> +#3.7/2#2.5
!- 9'(1) 3' 3' 3' 3'> = !-  9' 3'> +#3/#2.5 + !-  9'-5'> +#7/#2.5
!- 9'(1) 3' 3' 3'-3'> = !-  9' 5'> +#7/#2.5 + !-  9'-3'> +#3/#2.5
!- 5 (0) 1 ^0  0  0 > = !-  5  4 > +#5.7/2#2.11 + !-  5  0 > -3/2#11
                       + !-  5 -4 > +#5.7/2#2.11
!- 5 (0) 1  1  1  1 > = !-  5  5 > +#7/4#2.11 + !-  5  1 > -#3.5/4#11
                       + !-  5 -3 > +3#5.7/4#2.11
!- 5 (0) 1  1  1 -1 > = !-  5  3 > -3#5.7/4#2.11 + !-  5 -1 > +#3.5/4#11
                       + !-  5 -5 > -#7/4#2.11
!- 5 (1) 1 ^0  0  0 > = !-  5  4 > -3/2#2.11 + !-  5  0 > -#5.7/2#11
                       + !-  5 -4 > -3/2#2.11
!- 5 (1) 1  1  1  1 > = !-  5  5 > +3#5/2#2.11 + !-  5  1 > +#3.7/2#11
                       + !-  5 -3 > +1/2#2.11
!- 5 (1) 1  1  1 -1 > = !-  5  3 > -1/2#2.11 + !-  5 -1 > -#3.7/2#11
                       + !-  5 -5 > -3#5/2#2.11
!- 5  2  0 ^0  0 > = !-  5  4 > -1/#2 + !-  5 -4 > +1/#2
!- 5  2  2 ^2  2 > = !-  5  2 > +1/#2 + !-  5 -2 > -1/#2
!- 5 ^1  1  1  1 > = !-  5  5 > +#3.5/4#2 + !-  5  1 > -#7/4 + !-  5 -3 > -#3/4#2
!- 5 ^1  1  1 -1 > = !-  5  3 > +#3/4#2 + !-  5 -1 > +#7/4 + !-  5 -5 > -#3.5/4#2
!- 5 ^1 ^2  2  2 > = !-  5  2 > -1/#2 + !-  5 -2 > -1/#2
!-11' 1' 1' 1' 1'> = !- 11' 9'> +#7/4#3 + !- 11' 1'> -1/2#2 + !- 11'-7'> +#5.7/4#3
!-11' 1' 1' 1'-1'> = !- 11' 7'> +#5.7/4#3 + !- 11'-1'> -1/2#2 + !- 11'-9'> +#7/4#3
!-11'(0) 3' 1' 1' 1'> = !- 11' 9'> -19/4#3.11 + !- 11' 1'> +#7/2#2.11
                       + !- 11'-7'> +5#5/4#3.11
!-11'(0) 3' 1' 1'-1'> = !- 11' 7'> +5#5/4#3.11 + !- 11'-1'> +#7/2#2.11
                       + !- 11'-9'> -19/4#3.11
!-11'(0) 3' 3' 3' 3'> = !- 11'11'> +1/4 + !- 11' 3'> -#3.5/2#2.11
                       + !- 11'-5'> +3#3.5/4#11
!-11'(0) 3' 3' 3'-3'> = !- 11' 5'> -3#3.5/4#11 + !- 11'-3'> +#3.5/2#2.11
                       + !- 11'-11'> -1/4
!-11'(1) 3' 1' 1' 1'> = !- 11' 9'> -#3.5/2#2.11 + !- 11' 1'> -#5.7/2#11
                       + !- 11'-7'> -#3/2#2.11
!-11'(1) 3' 1' 1'-1'> = !- 11' 7'> -#3/2#2.11 + !- 11'-1'> -#5.7/2#11
                       + !- 11'-9'> -#3.5/2#2.11
```

```
!-11'(1) 3' 3' 3' 3'> = !- 11'11'> -#5/2#2 + !- 11' 3'> -7/2#3.11
                      + !- 11'-5'> -1/2#2.3.11
!-11'(1) 3' 3' 3'-3'> = !- 11' 5'> +1/2#2.3.11 + !- 11'-3'> +7/2#3.11
                      + !- 11'-11'> +#5/2#2
!-11'^1' 3' 3' 3'> = !- 11'11'> -#5/4 + !- 11' 3'> +#11/2#2.3 + !- 11'-5'> +#11/4#3
!-11'^1' 3' 3'-3'> = !- 11' 5'> -#11/4#3 + !- 11'-3'> -#11/2#2.3
                   + !- 11'-11'> +#5/4
!- 6  0  0 ^0  0 > = !-  6  4 > +#7/4 + !-  6  0 > -1/2#2 + !-  6 -4 > +#7/4
!- 6  1 ^0  0  0 > = !-  6  4 > -1/#2 + !-  6 -4 > +1/#2
!- 6  1  1  1  1 > = !-  6  5 > -#11/4#2 + !-  6  1 > +#3/4 + !-  6 -3 > -#3.5/4#2
!- 6  1  1  1 -1 > = !-  6  3 > -#3.5/4#2 + !-  6 -1 > +#3/4 + !-  6 -5 > -#11/4#2
!- 6  2  0 ^0  0 > = !-  6  4 > +1/4 + !-  6  0 > +#7/2#2 + !-  6 -4 > +1/4
!- 6  2  2 ^2  2 > = !-  6  6 > +#11/4#2 + !-  6  2 > +#5/4#2 + !-  6 -2 > +#5/4#2
                   + !-  6 -6 > +#11/4#2
!- 6 (0)^1  1  1  1 > = !-  6  5 > -#3.5/4#2.7 + !-  6  1 > +#5.11/4#7
                      + !-  6 -3 > +3#11/4#2.7
!- 6 (0)^1  1  1 -1 > = !-  6  3 > +3#11/4#2.7 + !-  6 -1 > +#5.11/4#7
                      + !-  6 -5 > -#3.5/4#2.7
!- 6 (0)^1 ^2  2  2 > = !-  6  6 > +3#5/4#7 + !-  6  2 > -#11/4#7
                      + !-  6 -2 > +#11/4#7 + !-  6 -6 > -3#5/4#7
!- 6 (1)^1  1  1  1 > = !-  6  5 > +#3.11/2#2.7 + !-  6  1 > +3/2#7
                      + !-  6 -3 > -#5/2#2.7
!- 6 (1)^1  1  1 -1 > = !-  6  3 > -#5/2#2.7 + !-  6 -1 > +3/2#7
                      + !-  6 -5 > +#3.11/2#2.7
!- 6 (1)^1 ^2  2  2 > = !-  6  6 > +#11/4#7 + !-  6  2 > +3#5/4#7
                      + !-  6 -2 > -3#5/4#7 + !-  6 -6 > -#11/4#7
!- 6 ^0  2 ^2  2 > = !-  6  6 > -#5/4#2 + !-  6  2 > +#11/4#2 + !-  6 -2 > +#11/4#2
                   + !-  6 -6 > -#5/4#2
!-13' 1' 1' 1' 1'> = !- 13' 9'> -#11/4 + !- 13' 1'> +1/2#2 + !- 13'-7'> -#3/4
!-13' 1' 1' 1'-1'> = !- 13' 7'> +#3/4 + !- 13'-1'> -1/2#2 + !- 13'-9'> +#11/4
!-13'(0) 3' 1' 1' 1'> = !- 13' 9'> -1/2#2.7 + !- 13' 1'> +#11/2#7
                      + !- 13'-7'> +#3.11/2#2.7
!-13'(0) 3' 1' 1'-1'> = !- 13' 7'> -#3.11/2#2.7 + !- 13'-1'> -#11/2#7
                      + !- 13'-9'> +1/2#2.7
!-13'(0) 3' 3' 3' 3'> = !- 13'11'> +1/#7 + !- 13' 3'> -#11/2#7
                      + !- 13'-13'> -#13/2#7
!-13'(0) 3' 3' 3'-3'> = !- 13'13'> -#13/2#7 + !- 13'-3'> -#11/2#7
                      + !- 13'-11'> +1/#7
```

$$|-13'(1)\ 3'\ 1'\ 1'\ 1'> = |-\ 13'\ 9'> +\#3.11/4\#7 + |-\ 13'\ 1'> +3\#3/2\#2.7$$
$$+ |-\ 13'-7'> -5/4\#7$$
$$|-13'(1)\ 3'\ 1'\ 1'-1'> = |-\ 13'\ 7'> +5/4\#7 + |-\ 13'-1'> -3\#3/2\#2.7$$
$$+ |-\ 13'-9'> -\#3.11/4\#7$$
$$|-13'(1)\ 3'\ 3'\ 3'\ 3'> = |-\ 13'11'> -5\#11/4\#2.3.7 + |-\ 13'\ 3'> +\#3/4\#2.7$$
$$+ |-\ 13'-5'> -\#5.7/4\#2.3 + |-\ 13'-13'> -\#11.13/4\#2.3.7$$
$$|-13'(1)\ 3'\ 3'\ 3'-3'> = |-\ 13'13'> -\#11.13/4\#2.3.7 + |-\ 13'\ 5'> -\#5.7/4\#2.3$$
$$+ |-\ 13'-3'> +\#3/4\#2.7 + |-\ 13'-11'> -5\#11/4\#2.3.7$$
$$|-13'(0)\hat{}1'\ 3'\ 3'\ 3'> = |-\ 13'11'> +\#5/4\#2.7 + |-\ 13'\ 3'> -\#5.11/4\#2.7$$
$$+ |-\ 13'-5'> -3\#11/4\#2.7 + |-\ 13'-13'> +\#5.13/4\#2.7$$
$$|-13'(0)\hat{}1'\ 3'\ 3'-3'> = |-\ 13'13'> +\#5.13/4\#2.7 + |-\ 13'\ 5'> -3\#11/4\#2.7$$
$$+ |-\ 13'-3'> -\#5.11/4\#2.7 + |-\ 13'-11'> +\#5/4\#2.7$$
$$|-13'(1)\hat{}1'\ 3'\ 3'\ 3'> = |-\ 13'11'> -\#11.13/4\#3.7 + |-\ 13'\ 3'> -\#3.13/4\#7$$
$$+ |-\ 13'-5'> +\#5.13/4\#3.7 + |-\ 13'-13'> +\#11/4\#3.7$$
$$|-13'(1)\hat{}1'\ 3'\ 3'-3'> = |-\ 13'13'> +\#11/4\#3.7 + |-\ 13'\ 5'> +\#5.13/4\#3.7$$
$$+ |-\ 13'-3'> -\#3.13/4\#7 + |-\ 13'-11'> -\#11.13/4\#3.7$$
$$|-\ 7\ (0)\ 1\ \hat{}0\ \ 0\ \ 0\ > = |-\ \ 7\ \ 4\ > -\#3.11/4\#5 + |-\ \ 7\ \ 0\ > +\#7/2\#2.5$$
$$+ |-\ \ 7\ -4\ > -\#3.11/4\#5$$
$$|-\ 7\ (0)\ 1\ \ 1\ \ 1\ \ 1\ > = |-\ \ 7\ \ 5\ > +\#3.11/2\#2.5 + |-\ \ 7\ \ 1\ > -1/\#2.5$$
$$+ |-\ \ 7\ -3\ > +\#3/2\#2.5$$
$$|-\ 7\ (0)\ 1\ \ 1\ \ 1\ -1\ > = |-\ \ 7\ \ 3\ > -\#3/2\#2.5 + |-\ \ 7\ -1\ > +1/\#2.5$$
$$+ |-\ \ 7\ -5\ > -\#3.11/2\#2.5$$
$$|-\ 7\ (1)\ 1\ \hat{}0\ \ 0\ \ 0\ > = |-\ \ 7\ \ 4\ > -\#7/4\#5 + |-\ \ 7\ \ 0\ > -\#3.11/2\#2.5$$
$$+ |-\ \ 7\ -4\ > -\#7/4\#5$$
$$|-\ 7\ (1)\ 1\ \ 1\ \ 1\ \ 1\ > = |-\ \ 7\ \ 5\ > -\#7/8\#2.5 + |-\ \ 7\ \ 1\ > -\#3.7.11/8\#2.5$$
$$+ |-\ \ 7\ -3\ > -\#7.11/8\#2.5 + |-\ \ 7\ -7\ > -\#5.13/8\#2$$
$$|-\ 7\ (1)\ 1\ \ 1\ \ 1\ -1\ > = |-\ \ 7\ \ 7\ > +\#5.13/8\#2 + |-\ \ 7\ \ 3\ > +\#7.11/8\#2.5$$
$$+ |-\ \ 7\ -1\ > +\#3.7.11/8\#2.5 + |-\ \ 7\ -5\ > +\#7/8\#2.5$$
$$|-\ 7\ \ 2\ \ 0\ \hat{}0\ \ 0\ > = |-\ \ 7\ \ 4\ > -1/\#2 + |-\ \ 7\ -4\ > +1/\#2$$
$$|-\ 7\ \ 2\ \ 2\ \hat{}2\ \ 2\ > = |-\ \ 7\ \ 6\ > +\#13/4\#3 + |-\ \ 7\ \ 2\ > -\#11/4\#3$$
$$+ |-\ \ 7\ -2\ > +\#11/4\#3 + |-\ \ 7\ -6\ > -\#13/4\#3$$
$$|-\ 7\ (0)\hat{}1\ \ 1\ \ 1\ \ 1\ > = |-\ \ 7\ \ 5\ > +1/4\#2.7 + |-\ \ 7\ \ 1\ > -\#3.11/4\#2.7$$
$$+ |-\ \ 7\ -3\ > -3\#11/4\#2.7 + |-\ \ 7\ -7\ > +\#13/4\#2$$
$$|-\ 7\ (0)\hat{}1\ \ 1\ \ 1\ -1\ > = |-\ \ 7\ \ 7\ > -\#13/4\#2 + |-\ \ 7\ \ 3\ > +3\#11/4\#2.7$$
$$+ |-\ \ 7\ -1\ > +\#3.11/4\#2.7 + |-\ \ 7\ -5\ > -1/4\#2.7$$
$$|-\ 7\ (0)\hat{}1\ \hat{}2\ \ 2\ \ 2\ > = |-\ \ 7\ \ 6\ > -\#13/4\#2.7 + |-\ \ 7\ \ 2\ > +3\#11/4\#2.7$$
$$+ |-\ \ 7\ -2\ > +3\#11/4\#2.7 + |-\ \ 7\ -6\ > -\#13/4\#2.7$$

```
!- 7 (1)^1  1  1  1 > = !-  7  5 > -#11.13/8#2.7 + !-  7  1 > -3#3.13/8#2.7
                       + !-  7 -3 > +5#13/8#2.7 + !-  7 -7 > +#11/8#2
!- 7 (1)^1  1  1 -1 > = !-  7  7 > -#11/8#2 + !-  7  3 > -5#13/8#2.7
                       + !-  7 -1 > +3#3.13/8#2.7 + !-  7 -5 > +#11.13/8#2.7
!- 7 (1)^1 ^2  2  2 > = !-  7  6 > +3#11/4#2.7 + !-  7  2 > +#13/4#2.7
                       + !-  7 -2 > +#13/4#2.7 + !-  7 -6 > +3#11/4#2.7
!- 7 ^0  2 ^2  2 > = !-  7  6 > -#11/4#3 + !-  7  2 > -#13/4#3
                   + !-  7 -2 > +#13/4#3 + !-  7 -6 > +#11/4#3
!-15' 1' 1' 1' 1'> = !- 15' 9'> -#7/8#3 + !- 15' 1'> -#3.11/8 + !- 15'-7'> -#7/8
                   + !- 15'-15'> -#5.13/8#3
!-15' 1' 1' 1'-1'> = !- 15'15'> -#5.13/8#3 + !- 15' 7'> -#7/8 + !- 15'-1'> -#3.11/8
                   + !- 15'-9'> -#7/8#3
!-15'(0) 3' 1' 1' 1'> = !- 15' 9'> -3#11/4#2.5 + !- 15' 1'> +#7/2#2.5
                       + !- 15'-7'> -#3.11/4#2.5
!-15'(0) 3' 1' 1'-1'> = !- 15' 7'> -#3.11/4#2.5 + !- 15'-1'> +#7/2#2.5
                       + !- 15'-9'> -3#11/4#2.5
!-15'(0) 3' 3' 3' 3'> = !- 15'11'> -#11.13/4#2.5 + !- 15' 3'> +#3/2#2.5
                       + !- 15'-5'> -1/4#2
!-15'(0) 3' 3' 3'-3'> = !- 15' 5'> +1/4#2 + !- 15'-3'> -#3/2#2.5
                       + !- 15'-11'> +#11.13/4#2.5
!-15'(1) 3' 1' 1' 1'> = !- 15' 9'> -7#7/8.3#5 + !- 15' 1'> -3#11/8#5
                       + !- 15'-7'> +#7/8#3.5 + !- 15'-15'> +5#13/8.3
!-15'(1) 3' 1' 1'-1'> = !- 15'15'> +5#13/8.3 + !- 15' 7'> +#7/8#3.5
                       + !- 15'-1'> -3#11/8#5 + !- 15'-9'> -7#7/8.3#5
!-15'(1) 3' 3' 3' 3'> = !- 15'11'> +#7.13/8.3#5 + !- 15' 3'> +#3.7.11/8#5
                       + !- 15'-5'> +#7.11/8.3 + !- 15'-13'> +#5.13/8.3
!-15'(1) 3' 3' 3'-3'> = !- 15'13'> -#5.13/8.3 + !- 15' 5'> -#7.11/8.3
                       + !- 15'-3'> -#3.7.11/8#5 + !- 15'-11'> -#7.13/8.3#5
!-15'(2) 3' 1' 1' 1'> = !- 15' 9'> -#5.13/4.3#2 + !- 15'-7'> +#5.13/4#2.3
                       + !- 15'-15'> -#7/2.3#2
!-15'(2) 3' 1' 1'-1'> = !- 15'15'> -#7/2.3#2 + !- 15' 7'> +#5.13/4#2.3
                       + !- 15'-9'> -#5.13/4.3#2
!-15'(2) 3' 3' 3' 3'> = !- 15'11'> +#5/4.3#2 + !- 15'-5'> -#11.13/4.3#2
                       + !- 15'-13'> +#5.7/2.3#2
!-15'(2) 3' 3' 3'-3'> = !- 15'13'> -#5.7/2.3#2 + !- 15' 5'> +#11.13/4.3#2
                       + !- 15'-11'> -#5/4.3#2
!-15'^1' 3' 3' 3'> = !- 15'11'> +#11/8#3 + !- 15' 3'> +#13/8
                   + !- 15'-5'> -#5.13/8#3 + !- 15'-13'> -#7.11/8#3
```

```
!-15'^1' 3' 3'-3'> = !- 15'13'> +#7.11/8#3 + !- 15' 5'> +#5.13/8#3
                    + !- 15'-3'> -#13/8 + !- 15'-11'> -#11/8#3
!- 8  0  0 ^0  0 > = !-  8  8 > -#5.13/8#2.3 + !-  8  4 > -#7/4#2.3
                    + !-  8  0 > -#3.11/8 + !-  8 -4 > -#7/4#2.3
                    + !-  8 -8 > -#5.13/8#2.3
!- 8 (0) 1 ^0  0  0 > = !-  8  8 > +#5.13/4.3 + !-  8  4 > +#7/4.3
                       + !-  8 -4 > -#7/4.3 + !-  8 -8 > -#5.13/4.3
!- 8 (0) 1  1  1  1 > = !-  8  5 > +#7.13/8.3#2 + !-  8  1 > +3#11/8#2
                       + !-  8 -3 > +#5.7/8#2.3 + !-  8 -7 > +#5.13/8.3#2
!- 8 (0) 1  1  1 -1 > = !-  8  7 > +#5.13/8.3#2 + !-  8  3 > +#5.7/8#2.3
                       + !-  8 -1 > +3#11/8#2 + !-  8 -5 > +#7.13/8.3#2
!- 8 (1) 1 ^0  0  0 > = !-  8  8 > -#7/4.3 + !-  8  4 > +#5.13/4.3
                       + !-  8 -4 > -#5.13/4.3 + !-  8 -8 > +#7/4.3
!- 8 (1) 1  1  1  1 > = !-  8  5 > +#5/2.3#2 + !-  8 -3 > -#13/2#2.3
                       + !-  8 -7 > +#7/3#2
!- 8 (1) 1  1  1 -1 > = !-  8  7 > +#7/3#2 + !-  8  3 > -#13/2#2.3
                       + !-  8 -5 > +#5/2.3#2
!- 8 (0) 2  0 ^0  0 > = !-  8  8 > +#7.11.13/8.4#3 + !-  8  4 > -#5.11/8.2#3
                       + !-  8  0 > -#3.5.7/8.2#2 + !-  8 -4 > -#5.11/8.2#3
                       + !-  8 -8 > +#7.11.13/8.4#3
!- 8 (0) 2  2 ^2  2 > = !-  8  2 > +1/#2 + !-  8 -2 > +1/#2
!- 8 (1) 2  0 ^0  0 > = !-  8  8 > -#5/8.4 + !-  8  4 > -#7.13/8.2
                       + !-  8  0 > +#11.13/8.2#2 + !-  8 -4 > -#7.13/8.2
                       + !-  8 -8 > -#5/8.4
!- 8 (1) 2  2 ^2  2 > = !-  8  6 > -1/#2 + !-  8 -6 > -1/#2
!- 8 (0)^1  1  1  1 > = !-  8  5 > +#3.11/8#2.17 + !-  8  1 > +#3.7.13/8#2.17
                       + !-  8 -3 > -#5.11.13/8#2.17 + !-  8 -7 > -#3.5.7.11/8#2.17
!- 8 (0)^1  1  1 -1 > = !-  8  7 > -#3.5.7.11/8#2.17 + !-  8  3 > -#5.11.13/8#2.17
                       + !-  8 -1 > +#3.7.13/8#2.17 + !-  8 -5 > +#3.11/8#2.17
!- 8 (0)^1 ^2  2  2 > = !-  8  6 > -#7.11/4#2.17 + !-  8  2 > -#3.5.13/4#2.17
                       + !-  8 -2 > +#3.5.13/4#2.17 + !-  8 -6 > +#7.11/4#2.17
!- 8 (1)^1  1  1  1 > = !-  8  5 > +#5.7.13/4#2.17 + !-  8  1 > -#5.11/4#2.17
                       + !-  8 -3 > +#3.7/4#2.17 + !-  8 -7 > -#13/4#2.17
!- 8 (1)^1  1  1 -1 > = !-  8  7 > -#13/4#2.17 + !-  8  3 > +#3.7/4#2.17
                       + !-  8 -1 > -#5.11/4#2.17 + !-  8 -5 > +#5.7.13/4#2.17
!- 8 (1)^1 ^2  2  2 > = !-  8  6 > +#3.5.13/4#2.17 + !-  8  2 > -#7.11/4#2.17
                       + !-  8 -2 > +#7.11/4#2.17 + !-  8 -6 > -#3.5.13/4#2.17
```

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